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Within each section current methodologies are reviewed, research needs are presented, and priorities for future research are discussed. In the final section, federal legislation for regulation of toxic chemicals in the environment is summarized and research efforts which will aid in formulation and implementation of laws and regulations are suggested.

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PROCEEDINGS OF THE WORKSHOP ON TRANSPORT AND FATE OF TOXIC CHEMICALS IN THE ENVIRONMENT

Norfolk, Virginia
December 17 - 20, 1978

Rizwanul Haque, Workshop Chairman
Office of Environmental Processes and Effects Research
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FOREWORD

One significant parameter which determines environmental exposure to toxic substances is chemical transport and transformation. Knowledge of chemical transport and transformation is a key factor in specifying protective measures and is becoming an important tool in regulating chemicals under various legislation. The Office of Research and Development of the U.S. Environmental Protection Agency held a workshop in December, 1978, to delineate research priorities in this essential area, resulting in this document as a product. The workshop addressed several broad categories including water, air, soil/ sediment, biota, modeling, and regulatory support.

This document is a functional summary of chemical transport and transformation state-of-the-art and research needs. This document will provide guidance to the Agency in designing research programs as well as defining the role of transport and fate parameters in testing and regulating chemicals. We hope that it will also be utilized by organizations outside the EPA in developing new ideas and techniques for defining environmental exposure of toxic chemicals.

Allan Hirsch

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Effects Research

PREFACE

Expansion of our technological society has resulted in an increased production and use of synthetic chemicals. Concern for the hazards posed by these chemicals has resulted in the enactment of legislation by the U.S. Congress mandated to the U.S. Environmental Protection Agency. The Toxic Substances Control Act of 1976 is one of the recent acts of legislation in this regard. Because use of synthetic chemicals is critical for the maintenance of the national economy, the disadvantages versus the benefits of using potentially hazardous chemicals must be carefully scrutinized. Since thousands of chemicals are currently in use and many more are being developed, the task of a cost/benefit analysis of each of these compounds is monumental. To expedite the regulation process, tests for the screening of potentially hazardous chemicals are being developed. These tests are intended to provide rapid, dependable detection of potentially hazardous chemicals.

In order to determine hazard, knowledge of exposure level--the extent to which susceptible individuals or biosystems will be in contact with the chemical--is requisite. Since the extent of hazard is usually dose dependent, accurate assessments of hazards must also include an expected concentration range.

Determination of exposure level in relation to ambient concentrations of chemicals in the environment requires transport and transformation data. Similarly, information concerning a particular chemical's mode of circulation and transformation, and where it will form sinks after release into the environment, is necessary to determine the safe levels of effluent discharge for that chemical. Based on the use of this transport and transformation information, first the exposure level then the risk posed at given levels of release of the toxicant can be determined. Thus, transport and transformation data are vital tools in chemical hazard assessment, and this important potential necessitates maximum development of this area. Many organizations are currently compiling information regarding transport and transformation of toxicants in natural systems, and increased communication among those working in this area can promote efficient development of research programs.

In pursuit of these goals, the Office of Environmental Processes and Effects Research (formerly Office of Air, Land, and Water Use) sponsored a workshop to promote communication and to delineate research needs in the area of transport and transformation of toxic substances. The workshop was held in Norfork, Virginia, December 17-20, 1978. Initial planning took place at the EPA with the involvement of the Office of Research and Development, Office of Pesticides and Toxic Substances, Office of Water and Waste Management and the Office of Air, Noise and Radiation. The workshop was divided into six (6) groups with the workscope of each group defined prior to the beginning of the workshop. Each group was directed by a non-EPA scientist serving as chairman and an EPA scientist as a lead person. Scientists active in the study of transport and transformation within industry, academia, and government agencies were selected and invited to participate in each group. The six areas consisted of (1) water, (2) air, (3) soil/sediment, (4) biota, (5) modeling and exposure, and (6) the regulatory aspect of transport and fate. The chairman, EPA lead person, and group members cooperated to produce a document concerning research priorities in the area of transport and transformation of toxic chemicals. The chairmen subsequently reconvened to discuss revisions of the document.

The objectives of this workshop were to address the state-of-the-art and to identify research needs in the area of transport and fate of toxic chemicals in the environment as related to (1) the testing and screening of toxic chemicals and (2) the development of a predictive technique for estimating exposure to toxic chemicals in the multimedia environments. These two factors are important considerations in defining the risks and hazards imposed by toxic chemicals to humans and the environment. Thus, these factors should be used in regulation by the U.S. Environmental Protection Agency of chemical pollutants under such legislative authorities as Toxics Substances Control Act, Federal Insecticide, Fungicide and Rodenticide Act, Resource Conservation and Recovery Act, Clean Air Act, and Safe Drinking Water Act, and Clean Water Act. The workshop did not address the issues of health and environmental effects of chemicals.

This document is intended to aid in the understanding of current work in the area of transport and fate of pollutants in the environment and to help clarify future research directions. We hope it will be useful to anyone interested in the processes of transport and transformation, and especially to those who use this information to assess hazards posed by introduction of toxicants into the environment.

Rizwanul Haque
Workshop Chairman

ABSTRACT

Presentations at the U.S. Environmental Protection Agency sponsored workshop on Transport and Fate of Toxic Chemicals in the Environment, conducted in Norfolk, Virginia, December 17-20, 1978, are documented. The six sections, corresponding to the sections of the workshop, derive from the efforts of ninety-three scientists from government, academia, and industry, and represent state-of-the-art understanding in transport and fate research in water, air and soil/sediments compartments; effects of biota on toxic substances; exposure assessment and modeling; and regulatory aspects of transport and fate research.

Within each section current methodologies are reviewed, research needs are presented, and priorities for future research are discussed. In the final section, federal legislation for regulation of toxic chemicals in the environment is summarized and research efforts which will aid in formulation and implementation of laws and regulations are suggested.

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1.0 TRANSPORT AND FATE IN THE AQUATIC ENVIRONMENT

1.1 INTRODUCTION

Recently, Congress has enacted legislation which requires the United States Environmental Protection Agency (EPA) to regulate many toxic chemicals in the environment. This regulatory pressure has begun to highlight fundamental inadequacies in the understanding of transport and transformation processes affecting the fate of chemicals in the water environment and the ability to properly assess exposure.

In an effort to clarify present research goals, the Office of Research and Development of the EPA invited prominent non-Agency scientists to discuss research frontiers in the area of aqueous transport and fate of toxic chemicals with EPA scientific/managerial officials. The participants were asked to identify the principal research obstacles to the prediction of toxicant fate and exposure and to attach relative priorities to these research needs.

Recommendations for high, medium or low priority research needs refer to a relative allocation of resources based on the adequacy of existing knowledge and environmental importance. Thus, some important but well understood processes have been assigned low priority. In such cases the group does not wish to imply less priority than at present.

The report reflects the strong consensus developed among the participants that development of our abilities to predict fate and exposure of toxic chemicals in the aquatic environment depends heavily on: (1) future research developments in the accumulation of reliable physicochemical property data; (2) increased understanding of dominant transport routes to and from the water column (especially for transport in the sorbed state and through the action of aquatic biota); and (3) continued development of our understanding of the kinetics of transformation processes in the aquatic environment. Important and unique needs were also identified for the special aquatic environment represented by ground and saline water. In addition, the participants concentrated on the characteristics of sources of toxic chemicals that most heavily influence fate and persistence, such as methodology for accurate total flux data, dissolved-particulate fractionation, particle size distribution, and chemical speciation.

1.2 PHYSICOCHEMICAL PROPERTIES

While there have been advances in the state-of-the-art technology, a need exists for standardization of testing to reconcile wide differences in the existing literature regarding physicochemical properties. In all discussions, it is assumed that the correct chemical structure of any organic material would be established and available, though this was not initially the case with Mirex.

1.2.1 Aqueous Solubility

Aqueous solubility is regarded as an essential property in any assessment. For solid nonionic materials the National Bureau of Standards (NBS) May-Wasik-Freeman "Generator Column" method (May et al. 1978a, 1978b) is preferred, though some doubt exists about its applicability to ionic solids, some halogenated hydrocarbons, and liquids. The Haque-Schmedding method is also excellent (Haque and Schmedding 1975). Further development work by NBS and others is strongly recommended to define procedures and scope, and to standardize methods.

Solubility is influenced by temperature, electrolytes, surface active agents, and possibly by natural organic substances such as fulvic acids. The magnitude of these effects should be elucidated, with fulvic acids given the highest priority.

For sparingly soluble compounds, accuracy within a factor of two is adequate but many published data are highly inaccurate. A standard compilation of critically reviewed data would be invaluable. Work on structure - solubility relationships should be pursued as a potential method of prediction and as a means of exposing bad data.

1.2.2 Octanol/Water Partition Coefficient (K_{OW})

This quantity is indicative of the tendency of a solute to partition into lipid phases and onto organic carbon in sediments (Leo et al. 1971; Neely et al. 1974; Kenega and Goring 1978; Karickhoff et al. 1979; and others). Method standardization is desirable because extremely inaccurate values may be obtained by poor techniques. The continued development work on the Hansch-Leo approach to calculating K_{OW} should be encouraged.

Measurement techniques using HPLC are promising but not yet fully validated. Further work is recommended, especially for screening water effluents, to identify the presence of high K_{OW} compounds. The applicability of K_{OW} to ionic species such as carboxylic acids, phenols, and amines requires better definition. Unresolved questions relating to an apparent "upper limit" to K_{OW} should be clarified. Methods development and further data acquistion are straightforward and can be accomplished with relatively low expenditures.

More expensive, and thus meriting higher priority, are continued efforts to relate K_{OW} to environmental behavior, notably bio-uptake, sorption and toxicity. Such work should not only attempt to elucidate these relationships but should clearly define any limitations or areas of nonapplicability. Since the correlations are based on data for moderately hydrophobic compounds, their reliability when applied to low or high K_{OW} compounds should be examined carefully as a matter of high priority. Due to their economy and usefulness, a risk exists that these correlations may be over-applied.

1.2.3 Vapor Pressure

Vapor pressure is an essential quantity for prediction of rate of loss to the atmosphere. Published data are often in disagreement by a factor of 10 or more (Spencer and Farmer 1978); an extreme example is lindane, for which the range was 3000. Static methods are satisfactory for reasonably volatile compounds, but gas saturation flow systems (Spencer and Cliath 1969) are preferred for low volatility compounds. A standard technique should be defined. Very little work correlating vapor pressure with chemical structure has been attempted. Such correlations would be useful and should be carried out. This topic merits medium priority.

1.2.4. Henry's Constant (H)

This quantity is the ratio of vapor pressure to solubility. For some sparingly soluble, low volatility, compounds direct determination by a stripping technique is preferable (MacKay et al. 1979). A simple test to determine the possible significance of volatilization would be very useful and should be devised. Determinations of H for actual waters containing other contaminants is advantageous since the effective H (based on total liquid concentration) may differ substantially from the distilled water value. Medium priority was assigned.

1.2.5 Ionic Properties

For substances (primarily inorganic) forming dissolved ionic species, work should be devoted to acid-base and solubility equilibrium measurement, complex formation, redox equilibria, and sorption. Complex formation and sorption should be given the highest research priority of the four ionic properties.

1.2.6 Complex Formation

Data on the potential of organic substances to complex, chelate (or to be chelated), or speciate in some unusual manner are desirable to elucidate any mechanism of solubilization or transport. Low priority was assigned.

1.2.7 Sorption

A knowledge of the potential for sorption of organics on sediments, biota, and suspended solids is necessary to study transport and fate of toxic chemicals in the aquatic environment. In particular, information on the fractions of the substance in sorbed and dissolved states is critically important for predicting or correlating behavior in the water column.

Work relating the sorption partition coefficient to sorbent properties such as organic carbon content is useful as a mechanism of generalization. Further correlation with K_{OW} appears possible (Karickhoff et al. 1979), but the scope and limitations require definition. A body of information is available for sorption on activated carbon which may be useful in discovering the relative behavior of various sorbates. The entire area of sorption equilibrium is regarded as high priority.

1.2.8 Accuracy and Physical Property Data

Considerable discrepancies exist in the literature for physical property data, and inaccurate values are still being reported. The effort required to obtain accurate and precise data is usually underestimated. The NBS and EPA should play a more active role in this complex and demanding area by supporting activities such as methods development, standardization, interlaboratory comparisons, use of standard reference materials, and the compilation and revision of available data. The acquisition of physicochemical data for toxic substances is demanding and expensive. Not all data should necessarily be of the same degree of accuracy. For example, a substance with properties similar to ethylene glycol will not volatilize from water significantly because of its high solubility and low vapor pressure (i.e., very low H), so an accurate vapor pressure is not necessary. Similarly, accurate sorption data may be unnecessary for freons. It is not immediately obvious what accurate data are required until some form of "sensitivity analysis" can be conducted. Such analysis can only be done if estimates for all data are available.

The implication is that it may be more economical to proceed through several levels of sophistication initially using estimated values (from correlations, for example) with experimental determinations made to an accuracy dictated by the sensitivity of the exposure to the physicochemical property. A great contribution in this area can be made by "evaluative models" (Baughman and Lassiter 1978). Since physicochemical data are inherently reproducible in contrast to other environmental data, there is no excuse for the present, less-than-satisfactory situation.

1.3 TRANSPORT PROPERTIES

1.3.1 Bulk Flow or Hydraulics

A detailed knowledge of the prevailing hydraulic regime is critical for any site-specific work. These sites include river flow, lake stratification, estuarine mixing, tidal flushing, storm behavior, oceanic currents, and ocean stratification. The time scales and dimensions of these mixing or diffusion processes, horizontally and vertically, will often require quantification. Such work should be on an ad hoc basis because little optimism exists that any significant quantitative generalizations will be possible. The qualitative site-specific generalizations are already established.

1.3.2 Transport in Sorbed State (Vertical and Horizontal)

The water column dynamics of solutes which are appreciably sorbed are believed to be strongly influenced or even dominated by processes such as sinking in association with such solids as mineral or organic matter and fecal pellets. Examples include hydrocarbon transport in copepod fecal pellets from surface waters to ocean sediments (a process which is orders of magnitude more rapid than simple particle settling) and PCB transport to lake bottoms following wet or dry deposition from the atmosphere. In estuarine waters the salinity change may induce flocculation or desorption, and density differences may cause stratification.

This entire subject area, including organic and inorganic solutes, is one of high priority and requires better quantification, especially regarding acquisition of data on pollutant fluxes in various water columns.

1.3.3 Release Rates from Sediments

Since sediments are often the repository of significant quantities of toxic solutes, a knowledge of their release rates and mechanisms is necessary for effective regulation. This information is particularly needed if sediment alteration processes are naturally possible as a result of severe storms, or are man-induced by dredging or stream-flow control. The need for parallel bio-and chemical-transformation work is also apparent. Medium priority was assigned.

1.3.4 Air-Water Exchange

Diffusive volatilization or absorption processes appear to be capable of reliable mathematical description, but validation is required in actual environmental water bodies. The role of sorption in volatilization rates should be examined further as should the effects of surface organic microlayers and the rates of spray transfer. Reliable data on transfer coefficients for lakes, oceans, and rivers should be gathered and correlated. Relationships to oxygen reaeration constants should be exploited. This area deserves medium priority for organic solutes and low priority for spray transfer processes.

1.3.5 Biotic Transport

The dynamics and equilibrium of the processes of uptake, degradation, metabolism, and accumulation of toxic substances by various levels of biota is an area of growing scientific concern. Cometabolism by mixed, continuous microbial cultures should be studied and the distinction between food web magnification (predator-prey) and equilibrium lipid partitioning deserves more attention. The potential for bioaccumulation should be the topic of more study, especially for solutes such as hydrocarbons where existing data may be inconclusive. High priority should be assigned to work with organics and medium priority to inorganics.

1.4 TRANSFORMATION PROCESSES

Procedures for prediction of environmental fate in aquatic systems which are based on measurements of specific transport and transformation processes have a reasonable conceptual foundation. Moreover, no good alternatives to this approach appear to be presently available. This conclusion offers a point of departure for examining some of the detailed assumptions made concerning important transformation processes for organic and inorganic chemicals. Current assessment procedures are concerned primarily with the fate of organic chemicals, and interest has focused on the specific reactions that will account for their transformations in freshwater (Smith et al. 1978; Mabey and Mill 1978). This section attempts to summarize the processes that control transformations of both organics and inorganics and to develop some generalizations for inorganic chemical processes to assist in developing fate assessment methods similar to those used for organic chemicals.

1.4.1 Transformations of Organic Chemicals

The following processes are believed to be major routes for transformations of organics in water:

- Hydrolysis by water, H_3O^+ and OH^-
- Photolysis by direct absorption of light in the solar region (>290nm)
- Oxidation by free radicals and singlet oxygen
- Microbially mediated transformations
- Reduction in anoxic systems.

In one kinetic treatment each process is expressed as a rate (equation 1) which is a function of the concentration of the chemical, an environmental parameter such as pH, biomass or oxidant level, and a rate constant characteristic of the chemical, the process, and the temperature.

$$-d(C)/dt = -R_n = k_n (C) \qquad (1)$$

For the case described by equation 1, C is the concentration of chemical and k_n is the rate constant. k_n usually depends on temperature and composition of the medium, while the total rate of loss of C is simply the sum of individual rates:

$$R_T = \Sigma R_n \qquad (2)$$

An additional simplifying assumption, that k_n is essentially constant during the measurement interval, converts equation 1 into a pseudo first-order expression:

$$-d(C)/dt = k_n'(C) \qquad (3)$$

There are questions concerning the validity of the foregoing assumptions such as the importance of including in the rate equations environmental parameters which can vary widely in aquatic systems and may not be considered as constants.

1.4.2 Metal Ion Catalysis of Oxidation and Hydrolysis

Square planar iron and cobalt complexes such as phthalocyanines are powerful catalysts for oxidation of sulfur dioxide and sulfide to sulfate in water, being effective even at 10^{-9} to 10^{-11} M (Hoffman and Lim 1979). These observations raise the question of whether iron and manganese complexed with natural organics might also prove to be oxidation catalysts for selected organic structures in both dark and light natural waters. Reliable information on the role of trace metals - especially iron, copper, and manganese - in oxidation needs to be developed both for fresh and marine waters.

Also needed are some careful measurements of hydrolysis rate constants for organic structures which are known to be susceptible to metal ion catalysts (such as copper ions) under metal ion-free conditions and in fresh and saline waters.

1.4.3 Microbially Mediated Transformation

There is a dearth of reliable data concerning the behavior of mixed culture organisms in the biotransformation of organic molecules in natural waters. The need to understand synergistic effects of mixed cultures such as cooxidation requires more emphasis, as does the need for more investigations at very low concentrations of chemicals in natural waters where natural organics are present in large excess.

Several other problems in biological transformation include the possible role of photosynthetic algae in transformations, the need for greater understanding of anaerobic transformations, and the need to recognize that fate and effects are bound together when considering interactions of microorganisms and chemicals. Of major concern in evaluating microbial transformation in streams and rivers is whether organisms in these water bodies can acclimate to trace levels of organics and, if so, by what mechanisms and over what periods of time.

1.4.4 Sediments

The role of aquatic sediment in transformations is largely ignored in current assessment procedures. Sediments serve only as reservoirs of sorbed organics, and models assume that no significant transformations occur during a sorbed state. Sorption is not generally considered a transformation process, although it does contribute to the total loss of material. There are suspicions that this assumption is at least partly incorrect, but specific data on the question are lacking. One example is the enhanced rate of microbial transformations observed when clay particles are added to dilute solutions of organics. Other evidence points to inhibition of microbial action in sediments where sorption into deep pores removed organics from the access of microorganisms.

1.4.5 Transformations of Inorganic Chemicals

Transformations of organic molecules in the environment almost always have zero or negative free energies and for practical purposes are irreversible. Kinetic parameters are needed to evaluate these processes quantitatively. However, transformations of metal ions, complexes, and anions are often very rapid and reversible. As a result, thermochemical estimates and models are valuable tools for understanding the speciation of inorganic chemicals among different complexation and oxidation states.

Despite many apparent dissimilarities between organic and inorganic chemicals, some parallels exist in transformation/transport processes, and the following processes must be considered in developing models for fate of inorganic chemicals:

- Oxidation and reduction
- Complexation
- Precipitation and dissolution
- Sorption to particulate matter
- Metal-organic identification, synthesis and cleavage
- Photochemistry
- Bioaccumulation of metals.

1.4.5.1 Oxidation/Reduction

Species such as Fe, Mn, Cr, Cu and As may be oxidized at rates that depend on their complexation states; Fe^{2+} oxidizes more slowly as the chloride complex, and the rate is therefore slower in marine environments. Some rates of oxidation are pH dependent (Stumm and Lee 1961). For the oxidation

$$Fe^{2+} \xrightarrow{O_2} Fe^{3+}$$

the rate law is

$$-d[Fe^{2+}]/dt = k[Fe^{2+}][O_2][OH^-]^2$$

Manganese is oxidized from +2 to +3 or +4 by O_2 under abiotic conditions (Morgan 1967), and the process is possibly mediated by microorganisms (Sorokin 1970). Cu^+ is so rapidly oxidized that it is unstable unless strongly complexed (Baes and Mesmer 1976). Some evidence exists that Fe^{2+} also has a role in oxidation of organics (Theis and Singer 1974). More remarkable is the possibility that Cr^{3+} is reoxidized to Cr^{6+} in coastal water (Jan and Young 1978). None of these oxidations are well understood, and some are slow enough that kinetic data are needed to properly describe the systems. The oxidation of HS^- to S^{6+} catalyzed by Fe and Co complexes has been studied in detail (Hoffmann and Lim 1979).

1.4.5.2 Complexation

The complexation of Pb, Cu, and Cd by naturally occurring organics needs additional study as does the hydrolysis of Cu. Among common divalent cations, Cu^{2+} exhibits the largest stability constants for natural organics. Rate constants for many complexation reactions are known, but there are significant gaps for trivalent metal species.

1.4.5.3 Precipitation and Dissolution

Knowledge of the state of inorganics as precipitates or in solution is essential for understanding their other reactions. Much more information on these processes is needed including pH dependence, anoxic/oxic dependence, and the influence of other ions (CO_3^{2-}, PO_4^{3-}) on their rates. The state of precipitates (i.e., amorphous versus crystalline) will control their apparent equilibrium solubilities, and rates of dissolution may confound thermochemical estimates. For a number of metal ions the solubility product constant for CO_3^{2-}, S^{2-}, and PO_4^{3-} complexes are not well known and are badly needed. A detailed review of physicochemical properties for Cd has been prepared (Baes 1973).

1.4.5.4 Bioconcentration of Metals

This process usually does not significantly affect the concentrations of metal ions available in the water column; however, complexation of metal ions into cellular materials can concentrate metals by 10^2 to 10^4 times their water concentrations and affect either the organism itself or other organisms higher in the food chain. Concentration is selective, pH dependent, and appears to compete with complexation by Cl^-, CO_3^{2-}, SO_4^{2-} and organics in water (Sunda and Guillard 1976).

1.4.5.5 Generalizations on Characterizing Inorganics and Their Fate

As a minimum, the following information is needed to characterize inorganic species in water: pH, temperature, oxygen level, ionic composition and concentrations (Cl^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, S^{2-}), sediment composition load, and size distribution. In some cases thermochemistry alone will suffice to calculate equilibrium species distribution attained in one to several weeks; but when speciation is required in shorter times, existing data on kinetics of precipitation are inadequate.

1.4.5.6 Organometal Synthesis

Synthesis of carbon-metal or metalloid bonds occurs in sediments via cobalamin complexes derived from biological sources (probably microorganisms). For example, $(CH_3)_2Hg$ is formed in both oxic and anoxic systems. Kinetic parameters for all metal-carbon forming reactions and their reoxidation are poorly characterized at present and require additional investigation to facilitate their use in fate models.

1.4.5.7 Photochemistry

Insufficient data are available on the photochemistry of aquatic inorganic species to warrant significant generalizations. However, some metal organic complexes photolyze with transformation of the organic structure, and limited data suggest that organic multidentate ligands, which bind strongly to Cu or Fe, may have photolysis rates which are greatly enhanced by the presence of metal ions (Lockhardt and Blakeley 1975). This process could also occur for metal ions bound to biomass.

1.4.5.8 Adsorption to Particulate Matter

The dominant factors governing the adsorption of trace metals and trace anions to particulates in water are pH, temperature, nature of the particulate phases, amount of surface available, and the overall ionic composition of the water. In general, particulates such as metal oxides, biological particles, and clays exhibit strongly pH dependent adsorption. The charge characteristics of the particles and their surface functional groups ($-OH$, $-NH_2$, $-COOH$) influence the intensity and extent of species binding. Competition for adsorption sites between minor and major metal species (e.g., Pb^{2+}, Cu^{2+} and Cd^{2+} versus Ca^{2+} and Mg^{2+}), and similar competition between minor and major anionic species (arsenate and selenate versus sulfate and phosphate) influence the degree of adsorption. The role of naturally-occurring organic materials (fulvic and humic substances) in affecting the adsorption of trace inorganic species is poorly defined. Interaction between trace metals and trace organic chemicals (e.g., Pb^{2+} and nitrilotriacetate) appears likely to affect the adsorption of each, but such behavior is not yet well understood. In general, the rates of adsorption-desorption processes for simple inorganic species are believed to be high, so that an equilibrium treatment provides useful prediction. Complex species may prove to be more slowly reacting.

1.4.6 Transformation Processes Summary and Recommendations

The basic kinetic approach to fate assessment of organics and inorganics is the only acceptable method presently available. Some questions remain concerning the detailed kinetic assumptions used in some models. The need seems evident for kinetic expressions which require explicit terms for environmental parameters or functions and their variation. Most of the processes recognized for organic fate assessment appear to be in a satisfactory state of development, but four areas are identified for additional study:

- Microbial transformations in dilute solutions with mixed cultures
- Sediment-promoted reactions for sorbed organics
- Metal-ion catalyzed oxidations, photolyses, and hydrolyses
- Transformations in marine or estuarine waters.

Transformations of inorganic chemicals differ from those of organics primarily in the possibility that one can predict speciation of dissolved inorganics using thermochemical models. However, many details of kinetic processes for inorganics in water remain obscure and will require additional study. These include:

- Oxidation by oxygen
- Formation and cleavage of metal-organic species
- Competitive sorption of cations and anions to particulate matter

- Effects of changing from fresh to marine waters on kinetics
- Equilibrium processes.

Test methods to evaluate kinetic constants need to be improved, and increased efforts should be made to use estimation methods for structure-reactivity and kinetic relations to place upper and lower bounds on rate processes. These two preliminary steps would minimize unnecessary testing in the laboratory.

1.5 TRANSPORT AND PERSISTENCE IN MARINE AND GROUNDWATERS

This section discusses those environments and aspects of transport and transformation which are not easily described by linear dynamic models. In particular, the emphasis is on dispersion of the pollutant and the adaptation of the environmental system to the impact of the pollutant. The only special methodological consideration in this section is sampling. Because of complicated ocean circulation, marine samples and particulate matter or living organisms have a wide variability. Therefore, in choosing analytical methods, the accuracy of the method need not greatly exceed the reproducibility of samples.

1.5.1 Marine Environment

There is no single "marine environment" because of the widely differing transport situations which prevail in different locations. However, the marine environment is not totally site-specific, and it is possible to identify five types of environments which may be ranked in order of decreasing energy of mixing.

Dispersion of wave action and mesoscale circulation dominate the open ocean environment. Environmental impact is minimal provided the amount of pollutant is not too large or chronic. This has been documented in the case of the Ekofisk Bravo blowout (Mackie et al. 1978; Johnson et al. 1978) and the Argo Merchant oil spill (Grose and Mattson 1977; Center for Ocean Management Studies 1978).

A high energy coastline with a rocky or sandy shore subjected to strong surf action and frequent storms will normally not retain much waterborne pollution. Pollution dispersion will be rapid unless there is a long calm period where floating material can be deposited at high-tide level (Owens 1978).

In a low energy coastline, sedimentation will be more prevalent and buried sediment will be occasionally uncovered and dispersed by storms. More biota (especially mollusks used for food) make this an area of greater concern as pollutants will linger in the environment (Hann 1977; Hess 1978; Gilfillan and Vandermeulen 1978; Sanders 1978).

Estuarine waters, a complex regimen of fresh water flowing into salt water compounded by tidal mixing, can result in unexpectedly long retention times provided there is no stormy weather or strong offshore current. Sedimentation is very important, and accumulation of toxic materials in sediments can proceed unchecked and undispersed for many years (Mann and Clark 1978; Teal et al. 1978). Storms or dredging can suddenly reintroduce these materials to the water. The high level of productivity of unpolluted estuaries and the high levels of human activity in urbanized areas and harbors make this an important region.

Some salt marsh and some freshwater wetland areas act as important purifiers of the marine environment, either as filters for material from rivers and terrestrial runoff, or as active centers of chemical and biological transformation (Keefe 1972; Nixon and Oviatt 1973; Valiela et al. 1973). These areas should be of high concern because little if any knowledge is available of the capacity of wetlands to absorb toxic materials or of when their ability to absorb toxic materials has been exceeded.

Additional topics on dispersion include bioturbation and riverine input. Bioturbation occurs when organisms live in the sediment and mix it by burrowing (Schink and Guinasso 1978). An outstanding example is the burrowing shrimp, Callanassia major, which lives in subtropical subtidal carbonate environments. A single animal can dig a burrow 1 meter deep and turn over 50,000 cm^3 of sediment a year (Morris et al. 1977). The result is a blurring of the sedimentary record and a rapid burial of recent material. This process may be diminished if the burrowing animals are vulnerable to pollutant damage.

The input of most materials from rivers to the marine environment is poorly known. The National Academy of Sciences study of petroleum in the marine environment noted the lack of data, but little has been done to remedy the situation (Van Vliet and Quinn 1977, 1978). Little if any information is available on the input of other toxic substances. Unknown is the residence time of such materials in surface waters before they reach the ocean and the flux of organic materials of different kinds to the sea, as well as the rate of degradation and dispersion. The answers to these questions will be site-specific, not only with respect to terrain and inputs but also with respect to transport processes involving sedimentation.

When one goes from a freshwater to a marine environment, simple chemical factors such as salinity, dissolved oxygen, and pH may undergo sharp changes. A change in salinity will modify the speciation of dissolved metals, especially important toxic metals (Pb, Hg, Cd) which form strong chloride complexes. Clay minerals which are cation exchangers modify the composition of their adsorbed material, exchanging cations when confronted by high concentrations of sodium ion. Flocculation and sedimentation may be rapid because of changes in surface charge. Dissolved oxygen is normally plentiful (except in relatively unusual anoxic basins such as deep trenches and the Baltic Sea) and represents a simplification over the easily depleted stream and lake systems characteristic of terrestrial waters. Almost all marine waters are within a few tenths of pH 8, which also makes the modeling process (Stumm and Morgan 1970) somewhat simpler than in fresh waters where pH may vary from 2 to 10.

Transport phenomena in the oceans are only beginning to be elucidated. Except for Gulf Stream eddies, which can be monitored by satellite, and the rare, large-scale international study such as the MODE program (Richman et al. 1977; Robinson 1976; Wunsch 1976), little is known about the circulation of the ocean on a scale of 100 m to 10 km, yet this is the scale that is most important for dispersion of pollutants. The motion of particulate material in the open oceans was assumed to be simple settling in a quiescent tank; now it has been established by the use of deep sea sediment traps (Honjo 1978) that the primary flux of material from the surface of the ocean to the surficial sediments is rapid (46 mg/m^2 day at 5367 meters in the Sargasso Sea), mediated by copepod grazing and excretion of fecal pellets which are large (hundreds of microns) smooth packages that sink at a rate of about a hundred meters per day. Thus, the sediments of the deep ocean are chemically more like the surface waters than they are like the nearby deeper waters. This discovery points out that scientists constantly must be on the lookout for unknown or unexpected pathways in describing or predicting the environmental fate of pollutants.

1.5.2 Groundwater

Presently, 20 percent of the nation's water for industry and domestic use is supplied from groundwater, but 50 percent of drinking water is of groundwater origin. Subsurface waters are currently rather free from pollution compared to surface waters, but if they were to become contaminated they would be exceptionally difficult to purify and probably remain contaminated for long periods. The recent landfill chemical leakage in Niagara Falls points to the potential long-term danger of subsurface water contamination. Most information and regulations concerning water pollution relate to surface waters. Laboratory or field studies seldom examine the special conditions which characterize groundwater such as methods of entry, unusual physical, chemical, and biological conditions, abnormal persistence, and possible chromatographic versus quasi-plug flow of water movement (American Water Works Association et al. 1973).

Pollutants can gain access to the groundwater via injection wells, landfills, surface mining, and rapid infiltration. Injection wells are used to prevent saltwater intrusion or subsidence and often use tertiary treated wastewater. These wells add water directly to the underground aquifer. Landfills are typically located near cities, which are normally near rivers and shallow aquifers. Landfills often penetrate into the water table and are possible sources of pollution leaking into the groundwater for years. Plastics in landfills have been shown to release phthalate esters into groundwaters and other refractory organics are probably released (Dunlap 1976). The Niagara Falls industrial landfill incident forced people to vacate their homes because of the slow leakage of toxic chemicals into an underground aquifer.

Surface mining is an increasingly important potential source of shallow aquifer contamination, because mining operations are often below the shallow water table. Shallow groundwaters can have a humic acid content from decaying surface plant matter, and these acids can have strong heavy metal chelating and organic leaching capacities which could lead to contamination of shallow aquifers near surface mines (Steelink 1977).

Land application of wastewater for treatment by rapid infiltration is encouraged by EPA. A biologically active mat is built up at the surface of the infiltration basin, and it is expected that this active layer will adsorb as well as decompose organics by bacterial action. Many aspects of this process should be examined, such as the effectiveness of the living mat to retain and decompose refractory organics, optional application/aeration periods as well as soil and climatic variations, and the relative kinetics of sorption versus biological degradation in the top few inches. In addition, little information is available on the adaptation time required for new sites to establish themselves biologically. If rapid infiltration for water treatment is to be encouraged, an important need exists for the evaluation of the associated chemical, engineering, and biological factors. This evaluation is critical because the infiltrated water often enters shallow flowing groundwater with downstream human uses and, because it is well water, it is assumed to be potable.

Insufficient attention has been given to the special physical and chemical conditions which exist in groundwater and which may affect transport, degradation, and biological activity. There is no UV light, so photolysis, important in surface waters, is not possible. Typically, the organic content of the subsurface soil is low, and thus absorptive mechanisms for refractory organics are probably not as important as in surface soils and sediment. Since groundwaters are normally anaerobic, oxidation is not likely. Also, if bacteria are present they must be anaerobes or facultative aerobes, and both generally degrade organic matter more slowly and less completely than aerobes (Metcalf and Eddy 1972). Because of the low potential BOD of most groundwater even anaerobic microbiological activity is probably limited. Most studies of microbiological activity have focused on aerobic organisms, while little is known about the microbiology and metabolism in anaerobic groundwaters. The importance of mineral redox couples, e.g., Fe^{2+}/Fe^{3+} or Mn^{2+}/MnO_2, in the decomposition of organics should be examined.

Sampling and analytical techniques for very low level materials are difficult, especially in deeper aquifers where suction type pumping is no longer feasible. There is a need for improved sampling methodology, particularly for trace level hydrocarbons (Dunlap 1977). Once developed, a coordinated sampling regime in space and time should be realized to establish the presence and movement of trace level contaminants about land application sites in various soil and climatic conditions.

1.5.3 Microbial Interactions with Toxic Substances in Marine Environments

Responses of microbial populations to continuous exposure from low levels of pollutants may differ from responses to "one time" introduction of these pollutants. Two distinct research approaches are needed to investigate the influence of microorganisms on the rates of degradation of the pollutant. In the first case, the resident microbial assemblage may have become adapted to the pollutant through selection for resistant strains and induction of enzymes capable of attacking the pollutant. For such situations relatively long term degradation studies using microcosms would be appropriate. Data are needed, however, regarding the length of exposure time necessary for population adaptation and the threshold concentrations (if any) of pollutants at which selection for resistant types and enhanced degradation rates will occur. Conversely, studies intended to give information on the response of pre-existing microbial populations to the presence of a toxic substance need to be designed to follow the initial rates of degradation and must therefore involve shorter time periods. The problems inherent in following short-term (minutes or hours) turnover of a pollutant in marine systems might be resolved by the development of radio-tracer techniques for those pollutants which are available in radiolabeled form.

Recent studies have shown conclusively that, with regard to microbial uptake and mineralization of organic compounds by marine microbial populations, the fate of the compound depends largely on the concentration at which it is present in water (Wright 1973). At very low concentrations, free-living bacteria appear to out-compete other components of the microbial assemblage for organic compounds. At much higher concentrations, organisms such as algae and bacteria attached to detrital particles compete more successfully (Wright and Hobbie 1965; Azam and Hodson 1977). Therefore, any experimental design for following the microbial fate of a compound must consider the concentration at which the substance is present in the environment. Degradation studies should be conducted over a wide range of pollutant concentrations if the substance concentration can vary.

Models for predicting the fate of a toxic substance in a marine system characteristically contain terms describing the contribution of microbial activity to the net loss of compound from the environment. These terms contain a factor which estimates the biomass of the microbial population. There are a number of techniques presently in use for determining microbial biomass including plate counts (Carlucci and Pramer 1957), particulate adenosine triphosphate (ATP) determination (Holm-Hansen 1973; Hodson et al. 1976), and total adenylate determination (Karl and Holm-Hansen 1977). All of these methods have severe limitations. For instance, plate counting of bacteria from seawater often under-estimates population size by a factor of 10^3 or more. Studies are needed which will identify the most reliable methods for estimating microbial biomass in seawater and sediments so models can be predicated on some standardized estimate.

Bacteria and other marine microorganisms accumulate substances from water both by adsorption and by "active transport" (Wright and Hobbie 1965; Hodson and Azam 1977). In the case of compounds which are merely adsorbed onto cell surfaces, the microorganisms are functioning merely as particles, transporting but not transforming the pollutant. Conversely, active transport into the cell often leads to metabolism of the compound. Studies assessing the importance of microbes to the fate of a toxic substance often do not distinguish between these two fundamentally different processes, and further work is needed to make such a distinction. It may be possible to classify toxic substances according to whether they are adsorbed onto or transported into microbial cells (or both).

Presently, there are no data on the residence times of microbial cells in marine systems. If marine bacteria which accumulate toxic substances rapidly grow and are preyed upon by higher organisms, a potential exists for the bacteria to serve as "links" in passing the substances to organisms at higher trophic levels, including man. If marine bacteria grow slowly or not at all in seawater and are insignificant as links in marine food webs, they may serve as terminal "sinks" for toxic substances retaining them until they are deposited in sediments, or metabolized to CO_2 and organic metabolites.

To date, nearly all studies of microbial degradation of organic substances in marine environments have been conducted under well oxygenated conditions.

Studies are needed which will give information on rates of degradation in oxygen depleted environments such as coastal sediments and salt marshes where the anaerobic microbial processes (fermentation, denitrification, sulfate reduction, and methanogenesis) predominate.

Studies of pollutant degradation in aqueous environments typically involve an initial concentration measurement, incubation period, and filtration followed by subsequent concentration determination. There has not been much uniformity with regard to the types of filter membranes used, and recent studies indicate that frequently utilized glass fiber filters retain only a few percent of marine bacteria (Hodson and Azam, unpublished data). Thus, subsequent concentration measurements include the sum of dissolved and "microbially associated" pollutant. Such methodology needs improvement and standardization.

A number of recent studies indicate that the concentrations of many organic compounds in surface films on seawater can be 3 to 6 orders of magnitude higher than in bulk seawater. Similarly, the density of bacteria in the surface microlayer is many times higher than that of bulk seawater (Odham et al. 1978). In such an organically enriched environment, microbial activity might also be expected to be many times higher than in bulk seawater. Perhaps a significant percentage of the degradation of certain toxic organics in seawater occurs in this microlayer. Existing data are conflicting; i.e., inhibition of microbial activity in this layer by UV radiation may negate the effect. More studies seem appropriate, especially considering the hydrophobic nature of the many important toxic organic compounds.

In any given marine environment, microbial processes play a significant role in determining the overall chemical condition of pH, E_H, oxygen availability, etc. If the presence of a toxic substance alters the rates of microbially mediated geochemical processes, then the physicochemical environment and fate of the substance will also be altered. It is essential to develop techniques for assessing effects of toxic substances on naturally occurring microbial biogeochemical processes. In the past, modelers have assumed that concentrations would always be below the levels at which microbial processes could be affected. The implications of the possible biogeochemical effects are too important to be dismissed with this assumption.

1.5.4 Recommendations for Further Study of Transport and Persistence in Marine Groundwaters

High Priority:

1. Present scientific understanding does not permit accurate prediction of the fate of any toxic substance injected into groundwater systems. This inability is particularly acute for substances needing photolysis, microbial action, or dispersion to render them innocuous. Research on the fate of such materials in ground water systems is badly needed.

2. Monitor groundwater and study mechanism of decay of toxic chemicals.

3. Study changes in distribution of pollutants between particulate and dissolved phases, as well as speciation of components, on transition from fresh to salt water.

4. Give considerations to and study the effects of ocean disposal of waste in high energy coastal regions.

5. Study adaptation of natural microbial populations to pollutants, and determine threshold concentrations at which selection for resistant types and enhanced degradation rates will occur. Radiotracer methods may be helpful in these studies of short-term processes.

Medium Priority:

6. Determine rates of microbial degradation in oxygen-depleted environments such as coastal sediments and salt marshes, and study such sites as possible areas for natural processing of less-toxic pollutants.

7. Degradation studies should be made over a wide range of pollutant concentrations since microbial processes are expected to be nonlinearly dependent on concentration.

8. Methods are needed for estimating microbial biomass in seawater and sediments so that models can be predicated on some standard estimate.

Long-term research topics related to the above:

9. Distinguish between uptake of pollutants by adsorption on microbial cell material and active transport into the cell which can lead to metabolism of the compound.

10. Investigate microbial activity in the sea surface microlayer and the influence of photolysis on this activity.

11. Determine residence times of microbial cells in marine systems.

12. Investigate the alteration of natural microbially mediated geochemical processes by the addition of pollutants. Improve methodology for pollutant studies involving filtration to separate microbial fractions from dissolved fractions.

1.6 SOURCES OF TOXIC CHEMICALS IN AQUATIC ENVIRONMENTS

1.6.1 Introduction

1.6.1.1 Flow and Mass Balance Concepts

The concepts of a mass flow of pollutants to and through different environmental compartments (water, air, sediments, soils, biota) and of a chemical mass balance for elements and compounds are essential features of any effort to accurately relate pollutant emissions to environmental exposure levels. An assessment of exposure level for a toxic chemical in an aquatic environment therefore demands identification of all important sources for the chemical and physical-chemical characterization of each source. The pertinent information for each source includes: total emission rate of flux of the chemical to the aquatic environment, the physical state of the chemical (dissolved, particulate, or gaseous in the source), and specific molecular forms or speciation.

1.6.1.2 Sources and Exposure Assessment

A rationale for predictive exposure assessment is summarized by the following scheme for a chemical in an aquatic environment:

Fluxes

SOURCES - - → TRANSPORT - - → TRANSFORMATION - - → FATE

(Physical Forms) (Species)

Environmental Exposures

The chemical mass balance concept may be expressed as:

$$\text{Accumulation} = \text{Inputs} - \text{Outputs} \pm \text{Transformations}$$

As discussed in Section 1.2 the physical-chemical state of inorganic and organic chemicals is important in determining environmental behavior such as transport rates, biological availability, reactivity, and toxicity. The resultant accumulation and exposure for an element, compound, or derived chemical species will generally depend upon input fluxes, transport out of the system, and decomposition and formation through reactions. Thus, it is impossible to reliably treat transport, fate, and exposure without a thorough knowledge of source identity, mass emission rates, and physical-chemical forms.

1.6.2 Source Identification

From a broad perspective, sources of toxic chemical flux to the environment can arise at one or more points in the material stream of chemicals including extraction, manufacture, transportation, use, accidental losses, discharge, and disposal (National Academy of Sciences 1977a). It may be necessary to identify a variety of different chemical sources for a specific aquatic environment. Distinctions between "point sources" and disperse or "diffuse sources" are standard. Significant examples of diffuse sources for the aquatic environment are atmospheric deposition of metals (Huntzicker et al. 1975), gas absorption, release of pollutants from sediments (Neely 1977), and chemical infiltration of ground waters from polluted rivers.

General methodology for treating pollutant flows in a region has been discussed by Davidson and Friedlander (1978) with respect to metals and by White and Friedlander (1978) with respect to the suspected carcinogens, benzo[a] pyrene and chloroform. Their work emphasizes that an inaccurate emission inventory for a region can sometimes result in failure to identify an important environmental pathway.

The example of lead (Pb) in Southern California is instructive (Patterson and Settle 1975). The mass balance for Pb in the coastal waters required input flux data for aerosol deposition, rain, wastewaters, storm runoff, and dry weather flows. The diffuse atmospheric sources accounted for ~35 percent of total inputs, while coastal wastewater discharges (point sources) accounted for ~45 percent, with river flows adding ~20 percent.

Not all chemical species are introduced directly to the water environment by primary emission from a source or transported via another environmental compartment. Transformation reactions among species represent secondary sources of hazardous materials in the aquatic environment. Important examples currently recognized include trihalomethane formation by chlorination of various organics (Barcelona and Morgan 1978), synthesis of methylmercury and other metalalkyl compounds (National Academy of Sciences 1977b), and reaction of nitrite with amines forming nitrosamines.

In the case of chloroform in the Los Angeles Basin, Barcelona and Morgan (1978) estimated from an analysis of mass flows that about 14 kg/day of chloroform are emitted to the atmosphere from primary sources, whereas 65 kg/ day are emitted from the secondary sources involving chlorination of water. Daily dose/exposures to chloroform via water and air were calculated at 21 μg, and 14 μg, respectively.

Via reactions with chlorine, the precursor organics in water are the sources of chloroform and other trihalomethanes. Thus, humic acids and other naturally-occurring organics have been identified as sources of a toxic chemical in water. In general, sources of reactive materials which may yield toxic substances need to be systematically identified.

1.6.3 Source Characterization

1.6.3.1 Fluxes

For each identified primary or seconday source of a toxic chemical to an aquatic environment one needs to know the total flux (g/hour, kg/day, etc.) of the actual chemical or its precursors. This information is necessary for a total element or compound mass balance in the system. However, it may not be sufficient for assessing transport, persistence, exposure and fate for any but purely conservative substances whose physical-chemical form is unchanged in the environment. Thus, for many chemicals attention must be directed to the physical states of an element, e.g., dissolved or gaseous versus particulate fractions, and to species present, e.g., oxidized versus reduced forms, inorganic versus organic or metallorganic compounds, free versus complex ions, and monomers versus polymers.

1.6.3.2. Dissolved Versus Particulate Fractions

Toxic chemicals may exist in particulate matter in an adsorbed, precipitated, solid-solution, or emulsified state. The size range may be wide or narrow. Information on the dissolved and particulate fluxes of chemicals from sources to aquatic environments is important in predicting transport, persistence and fate behavior. The need for such information is greater the longer the time scale for transfer between these fractions in comparison to the residence time of the chemical in the aquatic environment. Chemicals which are predominantly particulate at the source, and which tend to remain so with time, have a "robust" association with particulate matter. These chemicals will be deposited to sediments rapidly, have less availability to some biota, and will show a reduced tendency to volatilize. On the other hand, chemicals with a rapid particulate-solution exchange rate ("labile") will show little influence of their initial source characteristics once in the environment. Thus, the initial distribution in a source and the kinetics of particulate-solution interchange are important characteristics of any given chemical. There is considerable evidence for many organic and inorganic chemicals that a substantial particulate fraction exists for a variety of sources, especially effluents and sludges, as well as for rivers or estuaries with high suspended loads. Almost all available information on particulate chemicals in water is based upon filtration or sedimentation procedures. The distinction between "particulate" and "dissolved" has been operationally defined by means of membrane or other filters with sizes of separation on the order of 0.5 µm to 0.1 µm. Fundamental considerations, and experience with atmospheric particulate pollutants, suggest that information on the size distribution of particulate fractions of chemicals will allow more accurate predictions of transport and exposure in aquatic environments.

1.6.3.3 Implications for Chemical Analysis

Trace organic analysis and trace element analysis for source and ambient environmental samples must take cognizance of the existance of particulate and soluble fractions. Certain isolation procedures such as purging of volatile organics may be incomplete because of strong adsorption and slow release from particulate matter. It appears that present analytical methodologies for organic chemicals need to be critically examined with respect to the effectiveness of isolation procedures for chemicals in the particulate state.

1.6.3.4 Particle-Size Distributions and Toxic Chemicals

The use of 0.1 to 0.5 µm membrane filters to distinguish between dissolved and particulate fractions of a chemical is reasonable when essentially all of the chemical resides in particles of a size greater than the filter pore size. If the particle size distribution in a source extends well down in the colloidal range (particle diameters much less than 0.1 µm) and if adsorption holds a chemical in the particulate state, then it is predicted that the chemical will have a significant mass that will escape conventional filtration separation procedures. The joint particle-size and distribution for a chemical is an important piece of information in guiding the choice of analytical methods and prediting transport and fate in the wter environment, as it has proven to be in the atmospheric environment (Davidson and Friedlander, 1978; Abrott et al., 1978).

There is a need for a new research effort to identify both the form of particle-size distributions and the toxic chemical content of different particle-size fractions in sources and aquatic environments. It will be necessary to develop new sampling and separation procedures for sub-micron particulate fractions in order to obtain results of wide applicability. The findings of Hoffmann and Lim (1979) on the size fractions of copper, lead, cadmium, and carbon in surface waters obtained by ultrafiltration represent one point of departure. Their methodology might be extended to characterizations of other chemicals in sources. Ultracentrifugation is another method which should be explored more fully.

1.6.3.5 The Need for Chemical Species Information

For both organic and inorganic chemicals, the species present in the system can strongly influence transport, transformation, distribution, and biological effects. The number of organic chemicals of concern is far greater than the number of elements, and each organic chemical is a species in the present sense. Precursors of organic transformation and products of reactions represent additional organic chemical species with which to contend. Modern trace organic analysis procedures such as chromatography, mass spectroscopy, and other spectroscopic methods detect and quantitate on a species basis. While it is increasingly recognized that a number of distinct chemical forms of each element can exist in water, exposure assessment for aquatic systems has been based almost entirely on total elements for trace inorganic pollutants in water (Hoover 1978). The reason lies in present limitations in analytical capabilities to differentiate among species of most elements.

A species matrix for the elements arsenic, chromium, cadmium, lead, copper, nickel, zinc, mercury, nitrogen, and selenium would contain at least 40 distinct chemical species comprising oxidized and reduced forms, hydrolysis products, complex ions, polymers, precipitates, and organic derivatives. Solution species for elements are strongly dependent upon pH, redox conditions, and major anion and cation constituents. To an unknown degree, species are also dependent upon naturally-occurring and pollutant organic chemical constituents some of which are chelating agents. Solution speciation is linked to particulate-dissolved fractionations for many elements (Hoover 1978; Vuceta and Morgan 1978).

The need for species characterization in sources exists because physical-chemical forms provide initial-concentration conditions for transport-transformation fate models. For example, chromium can exist in wastewater effluents in two oxidation states, Cr(III) and Cr(VI). The Cr(III) may exist in solution as hydrolysis products and complexes or in a particulate state, either adsorbed or precipitated; Cr(VI) may be in solution or adsorbed (Morel 1975; Jan and Young 1978). The total flux of Cr to the water environment, F_{Cr}, may consist of $F_{Cr(III)\ part}$, $F_{Cr(III)\ diss}$, $F_{Cr(VI)part}$, and $F_{Cr(VI)\ diss}$. The individual fluxes are products of the total element flux and the different speciation fractions for the element in the source. If redox reactions and particulate-solution interchanges such as desorption and dissolution are slow with respect to transport processes, the initial speciation at the source will be preserved into the water environment.

Similar considerations, different in detail for each element and source, apply to essentially all elements and compounds. Available analytical capabilities for chemical species and a lack of kinetic information on many transformations presently limit detailed speciation-exposure predictions to very few elements.

1.6.4 Recommendations for Improved Source Characterization Methods

Significant gaps exist in availability of proven procedures of sampling, isolation, resolution, identification, and quantitation for both organic chemicals and inorganic species in aquatic sources. Adequate measurement techniques do not exist for many of the more than 100 organic chemicals which EPA must regulate. In principle, isolation procedures (purging, adsorption, ion exchange, liquid-liquid extraction, freeze drying, reverse osmosis, ultrafiltration), resolution techniques (gas and liquid chromatography in various modes), and identification-quantitation devices (flame ionization, electron capture, conductivity, microcoulometry, mass spectrometry, spectroscopy) can be applied in suitable combinations to yield methods for every organic chemical in water (Trussell and Umphres 1978). In fact, current analytical methods are often not as accurate as required nor are they standardized. An enormous effort of development and demonstration is now required to bring forward analytical methods which are acceptable in terms of detection, accuracy, and appliability to wastes, effluents, sludges, and natural waters.

Areas requiring critical attention are representative sampling of water containing volatile species, separation and resolution of particulate-associated chemicals, and the approximate methodological sensitivities to be used for chemical flux and material balance calculations. The National Organics Monitoring Survey quantitated two dozen organic chemicals, partly because analytical methodology existed for them. Heesen and Young (1977) noted that the normal collection and composition procedures lead to significant losses of halogenated hydrocarbons from wastewater samples. They estimated that current methods probably acount for but a small percentage of halogenated hydrocarbons in effluents. A more intensive program of analytical development is clearly needed.

Perhaps the highest priority need in sources research is the development and demonstration of methods which will yield accurate total flux data for chemicals of interest. Research should focus on sampling, isolation, and quantitation improvements. Accurate total fluxes are essential for predictive models. Research on measurements and models for dissolved-particulate fractionation and particle size distributions of toxic chemicals will be of significant value in developing improved transport-fate-exposure models. Chemical speciation of inorganic and organic chemicals in aquatic sources is needed for predicting transport, availability, and toxicity in the water environment. Analytical research is needed on complexation, oxidized versus reduced chemical forms, and organic derivatives of elements.

1.7 MODELING IN AQUATIC SYSTEMS

This section includes an identification of the transport and reaction mechanisms that can operate in aquatic environments, an assessment of the information needed to describe these mechanisms quantitatively, and an evaluation of research needs for the effective modeling of toxic substances in aquatic systems. The fate of the substances introduced into an environmental system depends on the rate of input, output, and reaction of the material within the system.

1.7.1 Inputs and Outputs

Inputs and outputs include transport by advection and dispersion, transport across land-water boundaries (point and nonpoint land-based sources), transport across air-water boundaries (atmospheric deposition, volatilization and dissolution, aerosol formation), and transport across sediment-water boundaries (deposition, resuspension, diffusive exchange). Characterization of these input and output rates involved the following:

- Advective transport - requiring description of large-scale fluid motions such as river and tidal flows;
- Dispersive transport - requiring description of smaller-scale fluid motion using dispersion coefficients determined from established empirical relationships or field measurements with tracers;
- Point sources - requiring description of source flows and total concentrations of pollutants. Knowledge of dissolved and particulate fractions is usually required and descriptions of temporal variations can be needed;
- Nonpoint sources - total pollutant loadings or fluxes, the partitioning between suspended and dissolved fractions, and temporal changes can require determination;
- Volatization and dissolution - analysis can use Henry's solubility coefficient, mass transfer coefficients at the air-water interface, and such factors as wind speed, water velocity, water depth, and temperature;
- Atmospheric deposition - this factor may require experimental determination in field situations or it can be an output from an atmospheric model of the transport and fate of the substance;
- Aerosol formation - the transport of toxic materials from the water to the atmosphere by the formation of aerosols appears to be uncategorized at this time;
- Deposition to sediments - this can be described experimentally with considerable effort. Deposition depends upon hydraulic flow regime and the physical properties of particulates, including their size, distribution, and density. Biological effects from such processes as zooplankton feeding may also be important. Sediment deposition is the principal removal flux of most nonconservative substances in aquatic systems;
- Suspension of sediments - this can be caused by man-made disturbances (ships, dredges) and by fluid flow such as storms. For anoxic sediments, pore waters may contain high soluble concentrations of

pollutants which then contaminate overlying waters. Iron and manganese in resuspended sediments can be important in transporting both organic and inorganic pollutants. These inputs are difficult to quantify at present;

- Diffusional exchange - oxic sediments can support organisms that mix the surface sediments (bioturbation), thereby enhancing vertical transport across the sediment water interface. Anoxic sediments may permit vertical transport by molecular diffusion only. These fluxes are not quantified at present.

1.7.2 Reactions

Important reactions of toxic substances within aquatic systems include hydrolysis, photolysis, sorption and desorption, oxidation and reduction, association and disassociation, precipitation, biological degradation and biological uptake or bioaccumulation. These reactions involve the following:

- Hydrolysis - description requires determination of rate constants and evaluation of effect of pH, temperature, and possible catalysts;

- Photolysis - evaluation includes determination of the absorption spectrum of the compound of interest at wavelengths greater than 290nm, quantum yield, and radiation intensity. Other factors affecting this rate are surface area, depth, competing absorbers such as particulates and humic substances, sensitization, and certain metals;

- Sorption and desorption - description utilizes sorption partition coefficients, the concentration of adsorbing solids, kinetic constants for adsorption and desorption, the charge of the adsorbing species, chemical characteristics of the solids, and the concentrations of other substances that can compete for adsorbing sites. The particle size distribution of the adsorbing solids can affect the concentration of surface area available for absorption and the rate at which these solids are removed from the system deposition. The rate of removal of the pollutant from the water column is related to the rates of supply and deposition of the adsorbing surfaces;

- Oxidation and reduction - evaluation uses kinetic constants, the concentrations of dissolved oxygen and other oxidants, consideration of catalysts including metals, acids and bases, and ultraviolet light, and determination of pH and temperature effects;

- Association and dissociation - description requires the thermodynamic constants for both ligand and metal interactions, knowledge of the concentrations of reacting and competing metals and ligands, evaluation of the effects of pH, temperature, ionic strength, and perhaps kinetic constants when polymerization may occur;

- Precipitation - description requires thermodynamic constants, the concentrations of species forming precipitates, evaluation of the effects of pH, temperature, and ionic strength, and consideration of the effects of particulates and of surface active agents such as humic substances;

- Biological degradation - characterization can use kinetic constants for the degradation of the substance of interest by acclimated organisms, determination of organism populations, and can require description of the acclimation period. Effects depend upon the electron acceptor available and will vary considerably with oxic and anoxic conditions. Temperature and pH effects can be significant. As in the cases of removal by deposition and by absorption, the environmental substance (in this case biomass) reacting with the toxic substance is controlled by the inputs of other materials to the system;

- Biological uptake - this may be assessed using a food web model with a resultant need for many additional coefficients. It may be possible to approximate biological uptake by laboratory measurements such as octanol-water partition coefficients.

1.7.3 Modeling Recommendations

It is not feasible or necessary to develop a single, comprehensive, general model for the transport and fate of every toxic substance that may have been or will be introduced into all of the diverse physical, chemical, and biological conditions occuring in aquatic systems. The main driving force for any model is the total input of sources to the system. The sources will be site-specific. Model predictions depend predominantly on source characterization. The second important class of factors is the output of the material of interest from the system. Outputs include deposition and volatilization in addition to advective and dispersive flows. All are site-specific and deposition is usually the most difficult to evaluate. Regarding reactions in the system, it is not likely that a single pollutant will require evaluation of all pathways. Some reactions, such as adsorption and biological degradation, are difficult to predict and are affected by other inputs into the system. It is also plausible that other reactions not described here can be significant.

The number and diversity of the described inputs, outputs, and reactions should not be a mathematical or computational problem in most cases. However, the measurement requirements for obtaining the fluxes and coefficients are large and probably overwhelming. It is useful to evaluate some reactions in laboratory experiments in order to determine their potential need for consideration in actual environmental models.

Table 1-1 lists the processes which have been judged to require further study to permit effective modeling of transport and fate of toxic substances in the environment.

TABLE 1-1. MODELING RESEARCH PRIORITIES

Highest Priority

Outputs by depositional processes

Inputs and outputs by resuspension of sediments

Sorption-desorption reactions

Biological degradation reactions

Inputs from nonpoint sources

Inputs and outputs by volatilization and dissolution

Significant Priority

Inputs from point sources

Inputs and outputs by diffusional exchange at the sediment-water interface

Inputs by atmospheric deposition

Hydrolysis reactions

Photolysis reactions

1.8 SUMMARY OF HIGH PRIORITY RECOMMENDATIONS FOR AQUATIC RESEARCH

A. Physicochemical Properties

1. Further development of methods for measuring solubility of solid non-ionic materials.
2. Influence of natural organic substances (especially fulvic acids) on aqueous solubility or apparent solubility.
3. Standardized compilation of critically reviewed data.
4. Relationship of K_{OW} to environmental behavior.
5. Effect of complex formation and sorption on the measurement of solubility equilibria for substances forming dissolved ionic species.

B. Transport Properties

1. Increased quantitative data on the influence of sorption on pollutant flux in water columns.
2. More information on the processes of uptake, degradation, metabolism and accumulation of toxic organic solutes by various biotic levels.

C. Transformation Processes

1. Microbial transformation in dilute solutions with mixed cultures.
2. Sediment-promoted reactions for sorbed organics.
3. Metal-ion catalyzed oxidations, photolyses and hydrolyses.
4. Transformations in marine or estuarine waters.
5. Oxidation by oxygen.
6. Formation and cleavage of metal-organic species.
7. Competitive sorption of cations and anions to particulate matter.
8. Effects of changing from fresh to marine waters on kinetics and equilibrium processes.

D. Marine and Ground Waters

1. Prohibit injection (or other types of disposal affecting groundwater) of any toxic substance needing photolysis, microbial action, or dispersion to render it innocuous.
2. Monitor groundwater and study mechanisms of decay.
3. Study changes in distribution of pollutants between particulate and dissolved phases, as well as speciation of components, on transition from fresh to salt water.
4. Give considerations to, and study the effects of, ocean disposal of waste in high energy coastal regions.
5. Study adaptation of natural microbial populations to pollutants, and determine threshold concentrations at which selection for resistant types and enhanced degradation rates will occur. Radiotracer methods may be helpful in these studies of short-term processes.

E. Sources of Toxic Chemicals in Aquatic Systems

1. Perhaps the highest priority need in sources research is the development and demonstration of methods which will yield accurate total flux data for chemicals of interest. Research should focus on improvements in sampling, isolation, and quantitation. Accurate total fluxes are essential for predictive models.

2. Measurements and models for dissolved-particulate fractionation and particle size distributions of toxic chemicals will be of significant value in developing improved transport-fate-exposure models.

3. Chemical speciation of inorganic and organic chemicals in aquatic sources is needed for predicting transport, availability, and toxicity in the water environment. Analytical research is needed on complexation, oxidized versus reduced forms, and organic derivatives of elements.

F. Modeling in Aquatic Systems

1. Outputs by depositional processes.

2. Inputs and outputs by resuspension of sediments.

3. Sorption-desorption reactions.

4. Biological degradation reactions.

5. Inputs from nonpoint sources.

6. Inputs and outputs by volatilization and dissolution.

The Aquatic Environment group participants are listed in Table 1-2.

TABLE 1-2. AQUATIC ENVIRONMENT GROUP PARTICIPANTS

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2.0 TRANSPORT AND FATE IN THE ATMOSPHERIC ENVIRONMENT

2.1 INTRODUCTION

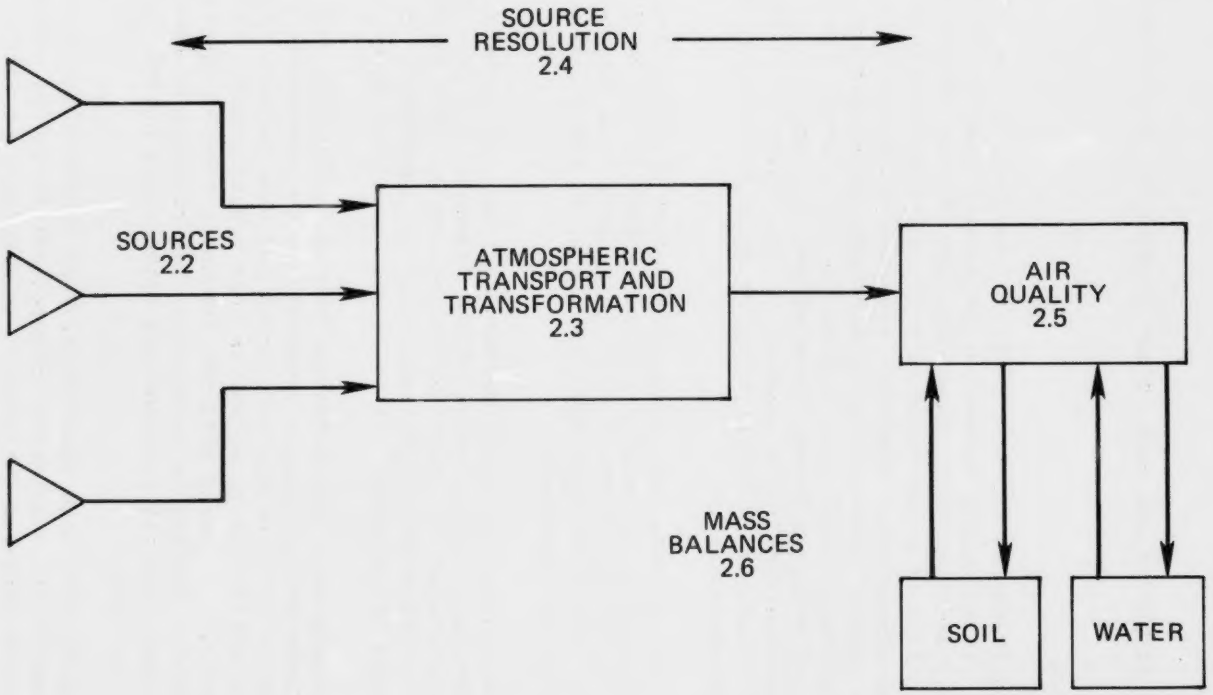
Research on transport and fate of toxic chemicals in the atmosphere concerns (1) the relationship between environmental quality and the various sources currently emitting toxic compounds, and (2) the effects upon environmental quality of a new technology or industry which will emit toxic chemicals to the atmosphere. Transport and fate parameters of toxic agents depend upon the agents' chemical and physicochemical properties; however, priorities for studying their flow through the environment should be based on their toxicity and emission rates. Much of the discussion in this section is devoted to recommendations for a research program designed to meet EPA needs in establishing regulatory guidelines for emission and control of toxic chemicals in the atmosphere.

Figure 2-1 illustrates how transport and fate problems were approached in this workshop and lists the general area of Section 2.0 which discusses the subject. The diagram traces the flow of pollutants from the source through the atmosphere where transformations may take place, to the point(s) where the air quality parameters are measured.

An emission source data base (Section 2.2) of high quality is essential to achieve a satisfactory understanding of the transport and fate of atmospheric pollutants. This element is sometimes overlooked and when programs on pollutant transport and fate are compartmentalized the atmospheric compartment is frequently treated (incorrectly) as if it were uncoupled from the source.

Rates of atmospheric transformation processes (Section 2.3) are needed to determine the lifetimes of organic compounds in the atmosphere. Such information can be used to guide source resolution and mass balance studies. In many cases it will be sufficient to establish that transformation rates are either very high or very low compared with the transport time of interest so that detailed information may not be necessary. The products of chemical conversion may themselves pose toxicity problems and methods are needed for predicting the nature of such products.

An air quality data base (Section 2.4) of research quality (as distinguished from routine air monitoring information) should be assembled. These data should include detailed information on chemical speciation for organic gases, aerosols, particle size distribution, and the distribution of chemical species with respect to particle size. The development of instrumentation necessary to accomplish this goal should continue.


SOURCE
RESOLUTION
2.4
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MASS
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WATER

FIGURE 2-1. FLOW OF TOXIC SUBSTANCES THROUGH THE ATMOSPHERE. (Numbers correspond to subsections with Section 2.0).

Research quality data are required for source resolution studies (Section 2.5) and environmental mass balances (Section 2.6) as well as for toxicity assessment. It may be possible to carry out source resolution studies for organic compounds using a chemical species balance method analogous to the chemical element balance (CEB) method developed for aerosol source resolution. A program of research should be initiated in this field using data available in the literature.

Mass balance studies are particularly useful for establishing the flow of a pollutant among various environmental compartments. Such studies should be initiated for organic compounds such as polynuclear aromatic compounds and halogenated organics.

While dealing with current air pollution poses many problems, an even greater task involves predicting the effects on environmental quality caused by introduction of new technologies or industries which release organic chemicals to the atmosphere. The ability to make such predictions will improve with the experience developed in treating existing sources. A good way to approach new sources will be by analogy with the methods discussed for treating existing sources.

These recommendations for research and development have attempted to strike a balance between basic research needs and the practical needs of the United States Environmental Protection Agency with associated time constraints. Recommendations for research have been limited to the direct needs of an integrated program on transport and fate and should be considered as minimum goals.

2.2 SOURCE CHARACTERIZATION

Recently a detailed picture of the characteristics of automobile emissions and emissions from pulverized coal-fired power plants has emerged with data on both the aerosol and gas phases available. Aerosols, particle size distributions, and chemical composition as a function of particle size have been obtained and a wide variety of organic compounds have been identified in automobile exhaust gases. These measurements have been made with advanced technology methods, sometimes especially developed for the purpose. Such data can be defined as research quality and are necessary for predictive modeling, source resolution, and mass balances. They are also needed for asssessing the health and ecological effects of air pollutants.

Few data of research quality are available for emissions from the chemical industry. There are many more types of chemical industry sources than automobile or power plant sources. As a result, it may be more difficult to generalize concerning the nature of such emissions. With proper measurements, it may be possible to generally characterize the emissions of a major class of sources, such as petrochemical plants, by doing detailed studies of just a few examples. Studies of this type have already been done in the case of particulate trace element emissions from several types of major sources. Coal-fired power plants are an example since there are great variations in the nature of emissions of a given element from one plant to another, depending on the type of coal used, the design of the boiler, the efficiency of pollution control devices, and stack temperature. However, detailed studies of a few examples of coal-fired plants (usually including measurements of the composition of the coal, various ash fractions, and suspended particles in the stack) have led to an understanding of the principles of fractionation of elements within plants such that with knowledge of the type of coal used and the plant design parameters one can now make reasonable estimates of emissions from a particular plant (see Davison et al. 1974; Klein et al. 1975; Kaakinen et al. 1975; Gladney et al. 1976).

Furthermore, it has been found that some types of sources that were a priori thought to be quite variable over time and from one plant to another were actually not so variable. For example, Greenberg, Zoller and Gordon (1978) and Greenberg et al. (1978) found that the composition of particles released from various municipal incinerators is quite similar and almost constant with time. The ability to treat most sources of a given class in a similar way allows formulation of reasonable chemical element balances by lumping sources of a given class (Section 2.4). Similar approaches may be successful in characterizing emissions of organic compounds from certain classes of sources without having to measure emissions on a plant-by-plant basis.

EPA sponsored field studies enlisting academic and industrial groups with different research capabilities have made important contributions to the understanding of the transport and fate of atmospheric pollutants. An example is the VISTTA (Visibility in Sulfur Transport and Transformation Areas) Project currently sponsored by the Agency. However, source characterization is frequently not carried out in conjunction with the field measurements; the laboratories which specialize in source measurements and field studies tend to work independently. When field studies of toxic organic compounds are sponsored by EPA, a strong effort should be made to include groups capable of careful source measurements (not routine air monitoring).

A detailed emissions inventory for atmospheric organics should be prepared based on available information and include the type of source and classes of organic emissions when more detailed information on chemical species is not available. The industry groups would be evaluated in the following descending order:

- Petrochemical based industry
- Metallurgical and inorganic chemical industry
- Coal based chemical industry
- Wood and cellulose based chemical industry
- Fossil fuel combustion
- Transportation

The emissions inventory should include not only industrial sources but also chemical waste dumps, pesticides, and other sources.

A major program should be initiated on detailed source characterization for the most important sources identified in the inventory. Priorities should be set based on toxicity and emission rates (Geomet 1977). Examples of possible sources are coke ovens and catalytic converters. Data should be obtained on chemical speciation for both the gas and aerosol phases. Aerosol data should include particle size distributions and distributions of chemical species with respect to particle size. Data should be of research quality using advanced measurement techniques and not of a routine air monitoring nature. The data should be of a quality sufficient for source resolution and mass balance studies. The source characteristics should be determined over time using a range of production conditions at a number of facilities to develop statistical information on the variability of the sources.

Measurements of source characteristics should be carried out in conjunction with field studies designed to measure atmospheric transport and transformation. Such integrated studies will enhance efforts to identify the complex pathways leading from pollution sources to uptake by humans.

An intra-Agency task force or committee should be established to provide direction on the priorities of chemicals and industries to be evaluated by the EPA. The counsel of the Science Advisory Board should be sought at an early stage. The Interagency Testing Committee's priority list of chemicals may offer direction though there are other chemicals of special interest to the EPA regulatory programs.

2.3 ATMOSPHERIC TRANSFORMATION PROCESSES

2.3.1 Atmospheric Lifetimes

The lifetime of a compound in the atmosphere depends on the compound's chemical reactivity in both the gas and aerosol phases, interaction with solid surfaces including vegetation, and solubility in aqueous phases taking chemical reaction into account. Section 2.3 discusses in some detail chemical reactivity in the air which also determines the generation of secondary products. The lifetimes of various organic compounds in air, based on chemical reactivity, are given in Table 2-1 along with comments on the feasibility of mass balance and smog chamber studies. A very long lifetime will lead to stratospheric sinks with dry deposition and washout becoming important. A short residence time such as a primary pollutant will increase the importance of studying the nature of the reaction products which may be present at high concentration in an urban and industrial region.

The toxicity, transformations, and sinks of any secondary products must also be considered. The transformation of a nontoxic chemical to a potentially toxic one is also a possibility. This transformation could be the case for polynuclear aromatic compounds, some of which are not initially active.

TABLE 2-1. TYPICAL RANGES OF ATMOSPHERIC RESIDENCE TIMES AND THE BOUNDARIES OF MASS BALANCE SYSTEM.

Compounds	R. T.	Scale	Loss Mechanism	Atmospheric Mass Balance Concept	Smog Chamber Studies
CCl_4, CCl_3F, CCl_2F_2, SF_6, CCl_2FCClF_2, etc.	50 year	Global	Photolysis in the stratosphere	Valid	Not useful
CH_3CCl_3, CH_4	3 year	Global	HO reaction	Valid	Not useful
CH_3Cl, $CHCl_3$, CH_2Cl_2	10 - 20 weeks	Regional	HO reaction	Valid	Most likely not useful
C_2Cl_4, C_4H_{10}, C_5H_{12}	1 - 2 weeks	Regional	HO reaction	Valid	Useful
C_2H_3Cl,C_2HCl_3, C_6H_6, C_7H_8, aldehydes, NO_x	2 days	Local	HO reaction/ photolysis	Some problems possible	Useful
Secondary products or highly short lived pollutants H_2S, C_4H_8, terpenes, NO, PANS, PPN, HO_2NO_2, Aldehydes	----	Will vary	Will vary	Not possible	Useful

2.3.2 Species and Processes Important in the Chemical Conversion of Organics

A useful approach to classifying compounds in terms of atmospheric chemical transformations is to consider their likelihood of participating in the following processes: (1) photolysis; (2) attack by hydroxyl radicals; (3) attack by ozone; (4) reaction with other radical intermediates, e.g., hydroperoxyl radical (HO_2), $O(^3P)$ atoms, etc.; (5) reactions with molecular species such as NO_x, SO_x, $O_2(^1\Delta_g)$, ground state oxygen, etc.; (6) hydrolysis; (7) thermal decomposition; and (8) aerosol formation and reactions.

If a compound undergoes photolysis in the actinic UV ($290 \leq \lambda \leq 410$ nm) or visible region it is important to characterize the resulting products and intermediates and to establish their individual fates in the atmosphere. Some of the key properties which need to be known are the UV absorption spectrum, the photolysis quantum yields in air, the products formed, and their rates of formation and decay (Pitts 1978).

It has been well established in the last five years that the OH radical is a key reactive intermediate in both the lower and upper atmospheres. For example, the dominant loss process for alkanes and alkenes as well as for many other organics in the polluted troposphere is attack by OH radicals (Demerjian et al. 1974; Falls and Seinfeld 1978; Atkinson et al. 1979). The rate of reaction of the chemical substances with OH radicals is critical for any study of atmospheric reactions. In a number of cases this reaction rate can be determined either experimentally or by comparison to similar compounds or both. Furthermore, it has been shown that reaction with OH can, in some cases, be indicative of the reactivity with respect to oxidant formation of a given compound and can be used as a means of classifying the reactivity of chemicals (Darnall et al. 1976; Pitts et al. 1976).

Reactions with ozone will be of major importance for unsaturated compounds. Unsaturated compounds with elevated levels of ozone can be competitive with or even exceed in importance reactions with OH (National Academy of Sciences 1977a, 1977b). Elucidation of the products of ozone-alkene reactions remains an important research area.

In general, organic reactions with HO_2 and with $O(^3P)$ at the ambient concentrations of these species will not be important relative to reactions with OH or ozone. Although present in photochemical smog at atmospheric concentrations of approximately 10^8 radicals cm^{-3}, HO_2 appears to react slowly with most organics (Graham et al. 1979). Conversely, while rates of reaction with $O(^3P)$ are fast (Hampson and Garvin 1977), its atmospheric concentrations are so low as to diminish its importance.

The radicals formed by attack by OH and other species are known to react subsequently with oxides of nitrogen and sulfur as well as with ground state molecular oxygen in many cases to form the ultimate products of photooxidation in the atmosphere. Thermal reactions with molecular species can also occur.

For chemicals and intermediates which may undergo hydrolysis it is necessary to determine rates and products at various humidities, both with and without aerosols, which may catalyze the reactions. In certain cases, thermal decomposition may be a significant factor in determining the stability and lifetime of a chemical in the atmosphere.

2.3.3 Predictive Modeling for Reactive Species

A methodology has been developed for the prediction of air quality from emission source data which accounts for transport (the wind field) and atmospheric conversion processes. The models have been developed with particular reference to photochemical smog and the prediction of ozone concentrations resulting from emissions of organics and nitrogen oxides under given meteorological conditions. Extensive reviews and comparisons of such models have been given in Ozone and Other Photochemical Oxidants (National Academy of Sciences 1977a) and Air Quality Criteria for Ozone and Other Photochemical Oxidants (U. S. Environmental Protection Agency 1978) and will not be repeated here. The results of such models should be of direct applicability to predicting reaction rates for organic compounds of interest. This applicability will be true for models which accurately predict the concentrations of reactive species such as OH radicals and ozone.

2.3.4 Hierarchy of Evaluation

The levels of evaluation of the fate of chemical substances in the atmosphere should be a function of usage, presumed toxicity, and emission factors. At least three degrees of complexity, involving the processes previously mentioned, can be suggested.

The first level consists of an initial screening procedure which would be based on a comprehensive assessment of the existing literature concerning the physical, chemical, and photolytic properties of a given compound. Available information such as the vapor pressure, structural groups, and absorption spectrum can provide a basis for estimating the likely paths and rates of transformation processes to determine the fate of an organic substance. Where such information is lacking it may be necessary to conduct fundamental laboratory studies to derive these basic properties.

A second level of evaluation would involve relatively straightforward and inexpensive experimental studies. An example would be the photolysis of a compound (including photooxidation), thermal reactions in the presence of oxygen, and (if any) hydrolysis reactions. At this level, simple irradiation experiments in small Teflon bags using typical ambient air pollutant concentrations could be conducted to obtain initial data concerning the nitrogen oxides (NO_x) photooxidation reactions of the chemical species. In such experiments, preliminary data can be obtained concerning both gas phase and aerosol phase products formed in such reactions. The rates of reaction and lifetimes may be determined by following reactant decay and mass balance. If the rate is very slow further chamber experiments would not be useful. Typical analytical tools which would be employed in such studies include: gas chromatography; wet chemical analysis; continuous gas phase analyzers for species such as ozone, NO, and NO_x; aerosol analyzers such as condensation nuclei counters; perhaps combined gas chromatography-mass spectrometry; infrared spectroscopy; thin layer chromatography; high pressure liquid chromatography; and analysis of the filtered reaction mixture. From these experiments basic reactivity and products estimates from the initial screening process may be verified and the need for further analysis determined.

If, on the basis of high usage or indications of substantial environmental impact, it is necessary to carry out complete and detailed assessments of the atmospheric transformations and fates of given chemical species having a significantly short lifetimes, an extensive program employing more sophisticated environmental chambers and other techniques such as flow reactors should be used. Analytical techniques such as long path FT-IR spectroscopy for the detection of labile compounds may be necessary.

When experimental evaluations of atmospheric transformations are required, it may be cost-effective to develop collaborative efforts between industry, university laboratories, and research institutes as well as governmental agencies to avoid unnecessary duplication of expensive experimental facilities.

2.3.5 Atmospheric Transformation Processes Recommendations

Based on hierarchy of evaluation, specific recommendations for the transformation of substances in air includes the following:

- Research should continue into tabulation and evaluation of rate constants for OH and O_3 reactions, evaluation of photolysis rates, and development of estimation schemes for atmospheric lifetimes of toxic substances. Additional experimental studies may be needed for key reactions or substances to validate estimation schemes.

- The elementary chemical kinetics of toxic substances or toxic substance precursors should be studied in detail. For substances which react rapidly in the atmosphere, survey type chamber studies should be undertaken and products identified.

- Protocols should be developed for testing potentially toxic substances in environmental chambers varying parameters such as HC/NO_x ratios, hydrocarbon composition, and presence of aerosols. Attention should be paid to mass balances in such experiments.

- Using literature and experimental data, predictive schemes for evaluating toxic products of atmospheric reactions based on a general atmospheric model should be developed. Existing models which predict gas and aerosol phase products of hydrocarbons with photochemical oxidants should be extended to new agents of interest.

- There is a need for kinetic measurements and chamber studies for the chemistry of aromatic compounds in the atmosphere because of the increasing aromatic content of unleaded fuel and the potential toxicity of the products. Ozone-olefin reactions to form toxic epoxides should also be studied.

- Substances which react slowly in the atmosphere or in some cases those which have fast homogeneous loss pathways may also be removed from the atmosphere through interaction with aerosol particles, vegetation surfaces, rain-out, washout, and dry deposition. Properties such as vapor presssure, solubility, and gas-surface interaction rates should be tabulated.

2.4 SOURCE RESOLUTION: CHEMICAL SPECIES BALANCES

Much progress has been made on the determination of the sources of suspended particulate matter in urban air with the chemical element balance (CEB) method. To use the CEB method one must know the elemental composition (for 20 or more elements) of particles released from all important sources in the area under study as well as the composition of ambient aerosols. The basic assumption of CEB is that the concentration of element $\underline{i}$ in a particulate sample is given by:

$$C_i = \sum_j m_j X_{ij} \qquad (1)$$

where $\underline{m_j}$ is the mass of material in the sample originating from source $\underline{j}$ and $\underline{X_{ij}}$ is the concentration of element $\underline{i}$ in material released by source $\underline{j}$ (Friedlander 1973). One usually performs a least-squares fit to the observed concentrations of a subset of the elements equal to or greater than the number of sources used in the fit to calculate the source strengths, $\underline{m_j}$ from a set of concentrations, $\underline{C_i}$.

For example, Kowalczyk et al. (1978) did a fit to eight elements (Na, Pb, V, Zn, Al, Fe, Mn and As) to determine the strengths of six sources (sea salt, motor vehicles, coal- and oil-fired plants, soil and municipal incinerators in the Washington, D.C., area. Ideally, elements used in the fit should originate mainly from one dominant source (Na, Pb, V and Zn from sea salt, motor vehicles, oil, and refuse combustion, respectively). However, soil and coal fly ash have such similar compositions that Al and Fe indicate the sum of the two, Mn is sensitive to soil, but depleted in coal emissions, and As is enriched in coal emissions.

The predicted concentrations of the measured elements not used in the fitting are compared with the observed values to test the reliability of the fit. Concentrations of many test elements were severely underpredicted in several early attempts to apply CEB (Friedlander 1973; Miller et al. 1972; Gatz 1975; Gartrell and Friedlander 1975) mainly because of limited information on the compositions of particles from important sources. However, in a recent CEB study of Washington, D.C., Kowalczyk et al. (1978) predicted 15 elements on the average to within a factor of two with most of the errors being underpredictions. Although this represents a rather good fit, work continues in various laboratories to eliminate some remaining weaknesses of the method. This additional work includes compositions of particles from additional sources that are important in some areas being determined (e.g., cement plants, steel mills, non-ferrous smelters), and separate CEB's being performed on small and large particles to allow for different residence times of different sized particles from a given source.

The CEB method works best for the primary aerosol components. For the secondary components such as NH_4^+, SO_4^{2-} and NO_3^-, it is necessary to have a gas-to-particle conversion model. Secondary components can also be treated using the statistical approaches of multivariate analysis, including factor and cluster analysis (Hopke et al. 1976; Henry 1977; Gatz 1978; Hopke 1977). For example, factor analysis makes no a priori assumptions about the number or composition of sources, but finds a minimum number of common factors that will explain most of the variation of concentrations from one sample to another in a large data set.

Although not totally complete, with the improvements and testing now in progress CEB and multivariate methods should soon be able to determine the magnitude of contributions of various sources to TSP and even the sources of most non-volatile elements on aerosols. There is less optimism about the ability of these methods to handle elements such as Hg, the halogens and, to a lesser extent, Se, which are so volatile that they may exchange with the gas phase depending on temperature, concentration, and the presence of reactive chemical species.

In view of the success of chemical element balances, an investigation of the applicability of a more general approach to chemical species balances (CSB) is recommended in which all chemical species (molecular and ionic species, elements, and both gas- and particulate-phase species) are used to establish relationships between sources and atmospheric concentrations. It is not a priori obvious that this approach is universally applicable to molecular species. The CEB approach has the advantage that elements are consevative; even though they may be transformed from one chemical form to another or from the gas phase to the particulate phase, one element does not transform into a different element. By contrast, if one attempts to apply CSB to a series of organic molecules released by various sources, one may find that the original concentration pattern is not conserved because some of the species may be transformed more readily than others into new species (Section 2.3). Nevertheless, the potential usefulness of CSB warrants an investigation of the possibilities.

The most obvious application of CSB to organic species would be to a series of closely related compounds. To be of value, the concentration pattern of species emitted should be strongly characteristic of each important source with large differences between types of sources. In order that the pattern be preserved between the time of release and the subsequent collection of samples, the various members should have comparable rates for major sink reactions, such as photolysis or attack by OH radicals. It would also be desirable for the volatilities to be such that all members of the series are mainly either the gas phase or the particulate phase.

Little has been done on the application of CSB to organic species but some classes of compounds appear promising, including the series of polynuclear aromatic hydrocarbons (PAHs). Although the PAH compounds differ considerably in vapor pressure, under ambient conditions most of them are probably in the particulate phase (though this may not be true at high stack temperatures). Futhermore, the pattern of PAH emissions from different types of sources is quite different, offering the possibility of source identification from the observed patterns (Gether and Seip 1979; Hites et al. 1977). Preliminary studies have, in fact, indicated that PAH patterns can be used for source identifications.

Other classes of compounds might be used in CSB. Mayrsohn and Crabtree (1976) have shown that the series of C_1 to C_5 hydrocarbons can be used to identify sources in the Los Angeles basin. In this case the compounds are in the gas phase. Other series which might be useful in CSB applications include organic halogen compounds, organic acids, and terpenes from natural sources, although the latter group may be too reactive over long distances from sources (Finlayson and Pitts 1976).

Another identification technique that may be helpful in identifying sources of carbonaceous species is the ratio of $^{14}C/^{12}C$ (or /total C). Carbon derived from fossil fuels is devoid of ^{14}C, whereas that from live or recently dead biological sources has a $^{14}C/^{12}C$ ratio in equilibrium with the atmosphere. The recently developed accelerator methods of $^{14}C/^{12}C$ measurements are much more sensitive than traditional ^{14}C β counting, making possible sensitive measurements with small sample sizes (Currie and Klouda 1979).

To test CSB for classes of organic compounds it will be necessary to make accurate measurements of the patterns in emissions from major sources of each class (Section 2.2). Care should be taken, especially in the case of sources with high temperature stacks, to insure complete collection of each species, including both gas and particulate phases. Furthermore, in testing the method in ambient air, it will be useful to measure not only the class of compounds of interest, but also trace elements characteristic of the sources (especially those found on small particles with long residence times). Since the major sources of many elements have been established, it will be possible to check some aspects of the CSB.

2.4.1 Sources Resolution Recommendations

CEB can be used to make reliable estimates of the sources of many toxic elements if they are not too volatile. Further refinements and application of the approach should be made. Improved methods for collection and measurement of volatile elements such as Hg, halogens, and Se are needed. When ambient samples are analyzed with a view towards CEB analysis, measurements should include Al and/or Ni, Mn and As as a minimum, or elements that are established as surrogates for these elements. Desirable additional elements for measurement include Fe, Ca, and Cd.

Some success has been achieved in the application of CSB to the identification of sources of organic species, but the method should be further tested on various classes of closely related compounds. When using CSB it is essential that measurements of hot sources include both gas and particulate phase emissions. As an additional test of this method it is recommended that simultaneous measurements of the elements noted using CEB be made since the sources of those elements are well established. Investigation should continue into the use of $^{14}C/^{12}C$ (or total carbon) ratios of carbonaceous materials to determine the ultimate source of carbon (i.e., fossil fuel or recent living material).

2.5 AIR QUALITY CHARACTERIZATION

Air quality characterization for atmospheric organic compounds requires the identification of such chemicals in the atmosphere and the separate measurement of their concentration in the gas and aerosol phases. The volatility and reactivity of certain organic compounds can make this task difficult. For example, pure benzo[a]pyrene (BaP), a compound of relatively high vapor pressure (Pupp et al. 1974) would be expected to be present in the gas phase at concentrations observed in the Los Angeles atmosphere. However, measurements confirm that BaP is present in the aerosol phase (Miguel and Friedlander 1978) probably as a result of adsorption on primary aerosol components. Compounds such as BaP when collected on a filter may also react with species in the gas phase as they are drawn through the filter.

Aerosol characterization requires information not only on the total concentration of the chemical species of interest but also its distribution with respect to particle size.

A careful characterization of air quality is necessary in studies of transport and fate for the following purposes:

- The estimation of atmospheric reaction rates (Section 2.3);
- The estimation of atmospheric scavenging by incloud processes and rain;
- The estimation of deposition rates on ground and vegetation;
- The completion of mass balances for various chemical species (Section 2.6);

The development of methods of measuring low concentrations of organic compounds in the gas and aerosol phases is an important part of a program for tracking the flow of toxic substances through the environment. Decisions on instrument development by EPA should be based on priorities set for specific classes of pollutants. Once specific agents have been chosen in the gas and aerosol phases, it will be easier to select the most appropriate types of measurement systems.

2.5.1 Air Quality Characterization Recommendations

Although many organic compounds have been detected and measured in the atmosphere, there is no central repository for the data. An inventory of data on atmospheric organic, organometallic, and volatile inorganic compounds should be established and include the name and chemical formula of the compound, concentration ranges, measurement methods, physical states (gas and/or aerosol), and measurement sites. Literature references should be cited and some measure of the quality of the data should be given. Because of the large number of candidate compounds and measurements, priorities should be set based on toxicity and emission rates (Geomet 1977). Where useful, compounds should be classed in family groups such as polynuclear aromatic compounds and halogenated organics. A limited inventory should initially be set up to gain experience.

Data for the inventory should be assembled from the literature and by surveying laboratories engaged in atmospheric chemical research. The information should be stored in an appropriate computer data bank from which the data could be retrieved and displayed in a number of ways (e.g., compound class, physical state, geographic location, temporal trends). This data bank would be maintained by EPA but would be available to the general scientific community. As new compounds are discovered and toxicity data developed, they would be added to the inventory.

Based on the inventory and toxicity information, a group of compounds should be selected for an atmospheric measurement program. Both gases and aerosols (in "respirable" and "non-respirable" fractions) would be sampled and analyzed. Measurement sites would be established at 5 to 10 locations around the country. Each site should be completely equipped with both sampling and analytical instrumentation (GC/MS, liquid chromatography, etc.,) and all chemical analyses would be done on-site. Sites would be chosen to represent different types of source impacts. If the sites are well chosen, the information obtained at this small number of sites will be applicable to other regions.

It would be desirable to have such sites located at academic institutions to maximize the research capability and the application of the results to air quality modeling (Section 2.3), source resolution (Section 2.4), and mass balances (Section 2.6). Because it is likely that the analytical system will contain a mass spectrometer with a computer data system, information related to compounds not on the survey list (or unidentified mass peaks) could be stored for retrospective study should the need arise. These data would be useful for a variety of purposes including epidemiological studies and chemical species balance research (Section 2.6).

United States Environmental Protection Agency should continue to support research on the development of new, highly sensitive methods for the detection and measurement of organic gases in the atmosphere. An essential part of such a program should be field applications of the new methods. The application of high resolution mass spectrometry and gas chromatography/mass spectrometry to atmospheric analysis has provided ample evidence for the merits of such exploratory studies.

While many methods of chemical sensing are available, priority in the development of instrumentation will be made by selecting the chemical agents of most concern to the toxic chemicals program.

There is evidence that the organic component of the aerosol contains carcinogenic constituents. Methods for the sampling and analysis of aerosol organics are primitive - even more so than for the inorganic components. Filters are usually used for sampling and the filtration process may result in changes in the chemical nature of the deposited material. Research should also be supported on the development of continuous, real-time methods of aerosol analysis for organics to avoid sample storage and delays in analysis.

More data are needed on the distribution of organic compounds with respect to particle size, particularly in the submicron size range. Such data are required for estimations of lung deposition and atmospheric loss rates.

Further studies of the biological effects of collected atmospheric samples should be made. Protocols and procedures should be developed for sample collection to maintain the activity of the sample of its atmospheric level.

2.6 MASS BALANCES

Mass balances between inputs to the atmosphere and outputs to other environmental compartments can be used to quantify the flows of pollutants through the environment. Such balances can be developed for geographic scales ranging from the urban to the global. The basic requirement is that the emissions to the atmosphere be balanced by flows out of the atmosphere. If a balance cannot be completed, the possibility of either an unknown source or an unknown environmental pathway must be considered.

Mathematically, the mass balance can be expressed as a series of simultaneous equations

$$C_i^\alpha = E_i^\alpha + D_i^\alpha + \Sigma_k T_{ki}^\alpha \qquad (1)$$

Where: C_i is the mass rate of accumulation of chemical α in environmental compartment i;

$E_i^\alpha = \Sigma_j E_{ij}^\alpha$ is the sum of emission of α from all sources j into compartment i;

$D_i^\alpha = \Sigma_r (D_{ir}^{(prod)} - D_{ir}^{(dest)})_\alpha$ is the sum over all chemical reactions r which either produce or destroy α in compartment i;

$T_{ki}^\alpha = T_{k \to i}^\alpha - T_{i \to k}^\alpha$ is the rate of mass transfer of α between compartments i and k.

The condition of mass balance requires that:

$$\sum_i C_i^\alpha = \sum_i (E_i^\alpha + D_i^\alpha + \sum_k T_{ki}^\alpha) \qquad (2)$$

In the absence of chemical reactions this reduces to:

$$\sum_i C_i^\alpha = \sum_i E_i^\alpha \qquad (3)$$

The types of information which are required for the construction of a mass balance are given in Table 2-2. Most mass balances appearing in the literature have used a combination of measured parameters or estimates based on such theoretical considerations as the relationship between particle size and deposition rate.

TABLE 2-2. TYPES OF INFORMATION NECESSARY FOR CONSTRUCTING A MASS BALANCE

Vapor pressure
Aqueous solubility
Identity of sources
Mass emission rate for each source
If aerosol, source particle size distribution
Ambient atmospheric concentration
If aerosol, ambient particle size distribution
Dry deposition rate
Rain-washout rate
Chemical reactivity in the atmosphere, soil, and water system
Sorption by particulate matter
Atmospheric transport rate from the region of interest

Once an acceptable mass balance is determined for a given chemical, it can be used as a model for predicting the environmental flows of chemicals with similar emission characteristics and chemical and physical properties. Such an analogy was used to predict the environmental flows of Mn if it were substituted for Pb in gasoline (Huntzicker 1975).

The geographic scale over which an atmospheric mass balance is feasible depends on the atmospheric lifetime of the pollutant (Table 2-1). For a highly reactive or easily removed pollutant, a mass balance would be possible only in a region localized around the source. For a substance with a lifetime of the order of days to weeks urban and regional scales can be used, and for pollutants with very long lifetimes global scales can be considered. In general, the atmospheric lifetime specifies the maximum extent of the geographic scale with all smaller scales also being feasible.

A partial list of mass balances which have been carried out for chemicals in the atmosphere is given in Table 2-3. The list can be divided into trace elements and organic compounds. Because the inherent identities of the trace elements are unaffected by chemical reactions, mass balances for these species are somewhat easier to construct than for organic compounds which can undergo a complex series of chemical reactions in all environmental compartments.

TABLE 2-3. MASS BALANCES FOR CHEMICALS IN THE ATMOSPHERE

SUBSTANCE	SCALE	REFERENCE
DDT	global	Woodwell et al. 1971
DDT	global	Cramer 1973
Hg	global	Xothny 1973
PCB	regional	McClure 1976
Pb	regional	Getz et al. 1977
Pb, Zn, Cd	regional	Van Hook et al. 1977
Pb	urban	Huntzicker et al. 1975
Zn, Cd	urban	Huntzicker and Davidson 1975
Benzo(a)pyrene	urban	Abrott et al. 1978

An example of a trace element mass balance is given in Figure 2-2 in which the flow of automobile emitted Pb is traced through the Los Angeles basin (Huntzicker et al. 1975). The input data were obtained from literature values for gasoline sales in California, the concentration of Pb in Southern California, the concentration of Pb in Southern California gasoline, and the

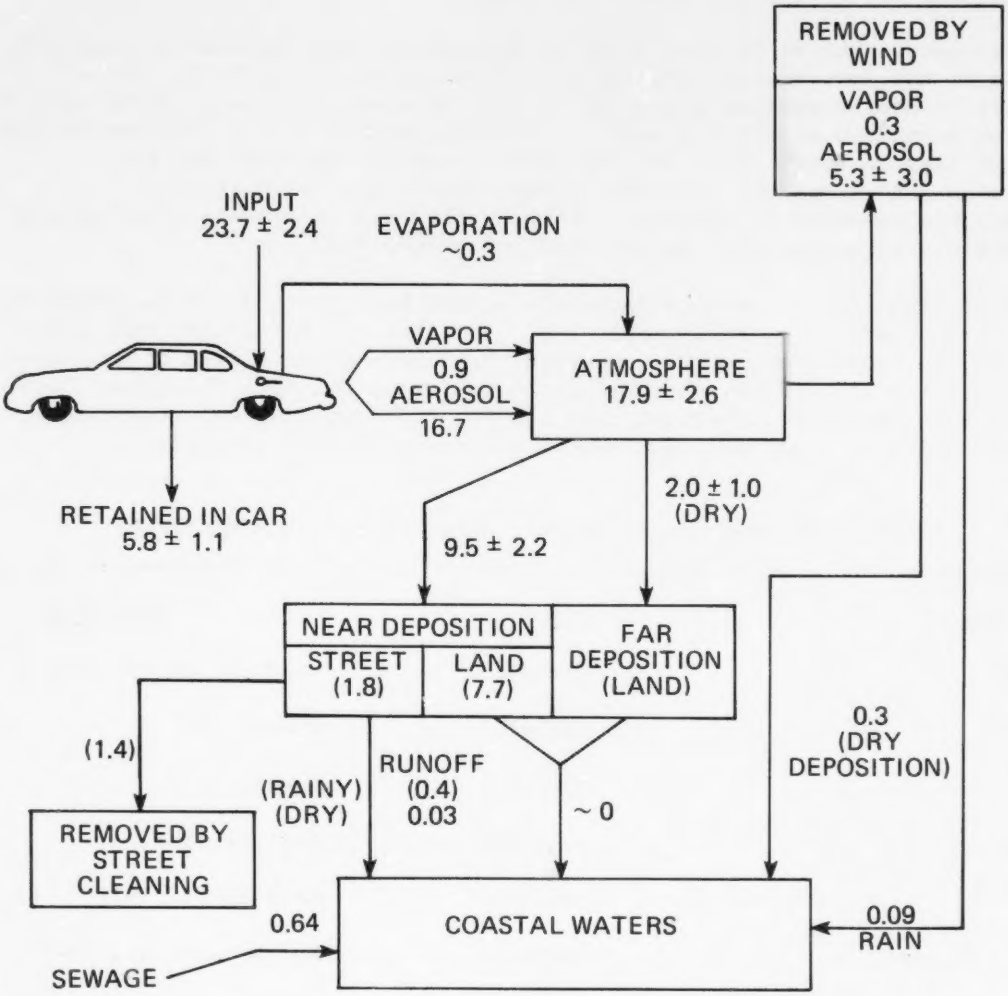
REMOVED BY WIND
VAPOR
0.3
AEROSOL
5.3 ± 3.0
INPUT
23.7 ± 2.4
EVAPORATION
~0.3
VAPOR
0.9
AEROSOL
16.7
ATMOSPHERE
17.9 ± 2.6
RETAINED IN CAR
5.8 ± 1.1
9.5 ± 2.2
2.0 ± 1.0
(DRY)
NEAR DEPOSITION
STREET
(1.8)
LAND
(7.7)
FAR DEPOSITION (LAND)
(1.4)
RUNOFF
(RAINY)
(DRY)
(0.4)
0.03
~ 0
0.3
(DRY DEPOSITION)
REMOVED BY STREET CLEANING
0.64
SEWAGE
COASTAL WATERS
0.09
RAIN

FIGURE 2-2. THE FLOW OF AUTOMOBILE EMITTED LEAD THROUGH THE LOS ANGELES BASIN. (With the exception of far deposition and wind removal fluxes, which are for dry weather only, the values are daily averages calculated by dividing the yearly totals by 365. All fluxes are in metric tons/day. Numbers in parentheses are model-dependent and in need of a more extensive data base. From Huntzicker et al. 1975a).

percent of consumed Pb exhausted to the atmosphere. Deposition near roadways was estimated from consideration of the known particle size distribution of auto exhaust Pb, and "far" deposition (away from sources) was measured. The amount of of Pb blown out of the basin was estimated by assuming the basin to be a continuously stirred flow reactor and using the relationship:

$$q_{Pb} = q_{CO} \overline{[Pb/CO]} \qquad (4)$$

where q_i is the mass flow rate of species i out of the basin and $\overline{[Pb/CO]}$ is the average value of the ratio of Pb to CO at receptor sites in the basin. Because CO is essentially unreactive on the urban time scale, $q_{CO}^{in} = q_{CO}^{out}$, and $q_{CO}/[CO]$ is a measure of the flow of air out of the basin. With this procedure it was estimated that 18±3 metric tons/day of Pb were emitted into the atmosphere and that the environmental pathways of near source deposition, far deposition, and removal from the basin by wind accounted for 17±4 tons/day. Because of the close agreement between input and output it is likely that all major sources and environmental pathways were included. The analysis also showed that the contribution of Pb from auto exhaust to the coastal waters was comparable to that from sewage.

A similar procedure was applied to Zn and Cd in the Los Angeles atmosphere (Huntzicker and Davidson 1975). More Cd was found in roadway deposition, far deposition, and removal by wind than could be accounted for by known sources. This suggested an unknown Cd source.

The situation with respect to toxic organic chemicals is considerably more complex than for most trace metals for the following reasons:

- Both photochemical and thermal reactions can transform the parent compound into more or less toxic daughter compounds (Pitts et al. 1978; Cliath and Spencer 1972).
- Significant reintroduction into the atmosphere of deposited compounds with low vapor pressure and low aqueous solubility can occur (Mackay and Wolkoff 1973; Spencer and Cliath 1975; Glotfelty and Caro 1975).
- Many organic compounds will exist in both the gaseous and particulate phases in the atmosphere.
- In many cases adequate analytical methodologies have not been developed.
- Adequate source information is often not available.

Because of these difficulties mass balances are available for only a few organic compounds (Table 2-2). Woodwell et al. (1971) and Cramer (1973) considered the global circulation of DDT, but because of the large number of assumptions involved in their models, some disagreement as to the importance of various environmental pathways occurred. One point which did emerge, however, is that the biological importance of a pathway can be much greater than suggested simply by the fraction of the total mass which flows through that pathway. Pathways carrying a small fraction of the mass can be very important from a biological standpoint and should not be overlooked.

Relatively little work has been done on the regional and urban flows of organic compounds. In a study of BaP in Los Angeles, good agreement was found between estimated BaP emissions and the amount of airborne BaP calculated from measured BaP/CO ratios during the winter and spring (Abrott et al. 1978). During the summer smog season much less than the expected amount of ambient BaP was found suggesting a chemical transformation of BaP with a half-life of about a day. McClure (1976) has studied the flow of atmospheric PCB's in Southern California by combining atmospheric concentrations and deposition measurements with a Gaussian puff dispersion model. An actual mass balance, however, was not possible because the source strength was not a priori known but was treated as a variable parameter.

2.6.1 Mass Balances Recommendations

The environmental flows of model compounds in both the gas and aerosol phases should be measured. Where appropriate, the environmental flows of other toxic compounds may be determined by analogy. Emphasis should be on organic compounds which comprise the bulk of known toxic substances.

Basic research in the following "interfacial processes" is needed, including: aerosol deposition processes; deposition of organic vapors; volatilization of organic compounds from realistic soil and water systems; and atmospheric detection of the volatilized compounds.

Studies should be conducted of the partitioning of organic and other volatile compounds between the aerosol and gas phases with specific attention to the role of sorption.

A complete mass balance for an organic compound for which substantial information is already available (BaP) should be worked up. The mass balance should take into account the effects of chemical reactions and the environmental flows of the reaction products.

Prototype mass balance studies of other selected organic compounds should be conducted. These would include compounds primarily in the vapor phase, compounds primarily in the aerosol phase, and compounds existing in both phases. Such mass balances should involve the determination of an emission inventory in the region of interest and measured mass flows of the compounds through the various environmental pathways. Such studies would follow from a mass balance for an organic compound with substantial available information and would provide a test of the applicability of the mass balance method to organic compounds.

The Air Group participants are listed in Table 2-4.

TABLE 2-4. ATMOSPHERIC ENVIRONMENT GROUP PARTICIPANTS

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3.0. TRANSPORT AND FATE IN SOILS AND SEDIMENTS

3.1 INTRODUCTION

Comprehensive assessment of the potential hazards of a contaminant within the environment requires detailed information on the distribution of dominant forms and related concentrations of the contaminant within each of the major environmental compartments: air, water, biota, soils and sediments.

Many contaminants exhibiting toxic, carcinogenic, mutagenic and/or teratogenic properties are known to associate strongly with soil and sediment materials via sorption phenomena. Soils and sediments thus function as significant sinks and sources in the transport and distribution of persistent contaminants. Further, such associations can have pronounced effects on chemical, physical, and biochemical transformations affecting the fate of contaminants, and on the bioavailability of parent compounds and transformation products to aquatic and terrestrial organisms, including man.

Association of a contaminant with soils and/or sediments frequently reduces the environmental hazard of the chemical. For example, it has been established that the percentage of total PCB content of water which tends to accumulate in fish is much higher in water bodies in low suspended solids than it is in waters having higher suspended solids content. Conversely, there are other chemical and/or biochemical reactions of adverse environmental impact which are promoted by such soil/sediment associations. For example, bottom-feeding organisms are exposed to high concentrations of contaminants in water bodies in which such associations have resulted in enriched levels of pollutants on solids at the sediment-water interface.

There is little doubt that the association reactions of contaminants with soils and sediments play dominant roles in determining the environmental behavior and significance of many of those contaminants of greatest potential concern. Any meaningful environmental hazard assessment program for a chemical contaminant must include an estimate of the extent to which that contaminant becomes associated with soils and/or sediments. This, in turn, is determined and controlled by a variety of physicochemical and biochemical phenomena, many of which are complex and interactive.

It is difficult to prescribe straightforward methodologies for the screening and testing of potentially hazardous compounds that will ensure precise prediction of environmental transport and fate. Nonetheless, it is necessary that methodologies be developed which afford at least a reasonable estimate of the major environmental characteristics of such compounds. With respect to the soil/sediment compartment of the environment, such methodologies must take account of at least the following important phenomenologic factors: a) the thermodynamics and kinetics associated with sorption/desorption processes, b) transport phemonena associated with leaching and exchange processes, c) photodegradation and volatilization, and d) physicochemical and biochemical transformations. The properties and characteristics of soils and sediments are important determinants of the relative extent and significance of these phenomena.

This chapter reviews state-of-the-art understanding of each of the phenomenologic factors identified as significant to the role of soils and sediments in the transport and fate of toxic chemicals in the environment, and considers major information deficiencies and selected research needs. In addition, these concerns are addressed in relation to meaningful characteri- tion of soils and sediments and their influences on the phenomenologic factors. Finally, land disposal of chemicals - one of the most direct routes of transport of toxic chemicals to this compartment of the environment - is considered.

It should be noted that the factors considered in this chapter are complex and interactive, that the body of contributors - although representing a reasonable breadth and depth of related knowledge and experience - does not necessarily constitute one of comprehensive expertise on all aspects of these factors, and that the time alloted for development of the dicussion was short. This report is not advanced as a totally exhaustive and definitive document and should not be taken as such. Rather, it is an attempt, constrained by the factors mentioned above, to provide one contribution to better definition of research needs relating to the role of soils and sediments in the transport and fate of toxic chemicals in the environment.

3.2 SORPTION-DESORPTION PROCESSES

Extensive work on the sorption of synthetic organic chemicals from water has been done in the past decade, and much has been learned about factors which affect and control the sorption of such compounds. Much of this effort has focused on the use of activated carbon for purification of drinking and waste waters, but many of the findings with respect to concepts and sorption dynamics can be extrapolated to naturally occurring soils and sediments. Detailed descriptions and discussions of sorption concepts and dynamics have been given by Weber and colleagues (1972, 1977, 1978, 1979a), are readily available in the literature, and will not be repeated here.

Much of the sorption work regarding the effects of potentially toxic compounds on soils and sediments has related to pesticides (Bailey and White 1964; Bailey et al. 1968; Lotse et al. 1968; Shin et al. 1970; Adams and Li 1971; Helling 1971; Goring and Hamaker 1972; Weber 1972). These studies have included characterizations of the effects of pesticide properties (pK_a, pK_b, water solubility, polarity) and soil properties (class, size distribution, organic matter content). With respect to chemicals other than pesticides, detailed studies have been performed by Haque et al. (1974) and Weber et al. (1979b) on the kinetics and equilibrium aspects of sorption-desorption reactions of polychlorinated biphenyls (PCB's) on different types and sizes of sediments, and on suspended soils under different solution conditions.

Sorption equilibria have been most commonly described in terms of the Freundlich sorption isotherm equation:

$$q_e = K_F \, C_e^{\;1/n} \qquad (1)$$

where q_e is the amount of contaminant sorbed per unit amount of sorbent, C_e is the equilibrium solution concentration of the contaminant, and K_F and $1/n$ are characteristic constants relating to the extent and intensity of sorption, respectively (Weber 1972).

While a variety of methods are available to determine distribution coefficients from sorption isotherms, laboratory batch tests of the type recommended by the American Institute of Biological Sciences (A.I.B.S. 1974) and cited by the U. S. Environmental Protection Agency (1975) are generally satisfactory.

For natural aquatic systems in which the ratio of quantity of contaminant to soil and/or sediment is low, the value of the constant 1/n in Equation 1 approaches unity, and the relationship between q_e and C_e approaches linearity. Sorption in these systems is frequently described in terms of the empirical equation:

$$S = K_d C \qquad (2)$$

where S is the sorbed concentration (in µg/g), C the solution concentration (in µg/g~µg/ml), and K_d the dimensionless "sorption coefficient" or "partition coefficient".

One of the most important factors affecting the partitioning of many pesticides and PCB's between soil or sediment and water is the organic content of the soil or sediment. Therefore, it is frequently useful to normalize sorption partition coefficients in terms of the organic carbon content of the sediment or soil. A "sorption constant" (K_{oc}) is defined as the amount of chemical sorbed per unit of organic carbon (in ppm) divided by the concentration of the chemical dissolved in the water (in ppm). Although this normalization is found to be applicable to a large number of organic compounds, especially nonionics, it is not universal.

A recent study (Karickhoff et al. 1979) of the sorption of toxic compounds from water onto sediment/soil suspensions produced the following generalizations for natural (dilute) aquatic systems:

1. The sorption of contaminants occurs to about the same extent on sediments and soils.

2. When normalized by the carbon content of a sediment or soil, the sorption of neutral organic compounds on sediments or soils from different areas varies by a factor of only 2 to 3. This conclusion, if substantiated by additional studies, could greatly simplify prediction of the sorption behavior of toxic organic compounds since the results of tests conducted on one, or a few, sediments or soils would in general be applicable to natural water systems throughout the world.

3. While the sorption of most toxic organic compounds on natural particulate matter is generally rapid (approaching near-maximum levels within a few hours) and reversible, there is an indication of continuing slow sorption. Further, there are some compounds which apparently do not desorb, or do so only very slowly.

4. In general, sorption on natural particulate matter has a low temperature coefficient (low activation energy).

5. One of the most promising developments is the correlation between the distribution coefficient for the uptake of neutral organic molecules by natural water solids and the octanol/water partition coefficient. A relationship of this type is to be expected for a large group of organic chemicals, especially nonionic compounds.

3.2.1 Sorption-Desorption Recommendations

Sorption studies to date have yielded some important tentative conclusions which may greatly facilitate prediction of the environmental behavior of contaminants which tend to associate with soils and sediments. A case in point is the observation that sorption frequently correlates well with the organic matter content of soil or sediment. The limitations of these conclusions should be determined for various classes of organic compounds in association with various types of sediments and soils. Where deviations are found for certain groups of organic compounds, studies should be conducted to develop generalizations applicable to that group relative to their uptake and release from natural fresh and marine water sediments, soils, and particulate matter.

For specific situations involving evaluation of the behavior of a particular contaminant at a certain location, soils or sediments from the area of interest should be used. However, in situations where attempts are being made to predict the environmental behavior of a chemical which is expected to have broad distribution in the environment, soils and sediments typical of those found throughout the United States should be used. Reference soils and/or sediments should be incorporated in testing schemes to develop a broad data base which can be used to estimate the environmental behavior of new chemicals.

Most existing information concerning the sorption behavior of toxic chemicals on soils has been obtained in experiments of relatively short duration, and for systems with water/soil ratios much higher than those encountered in field situations. Further, under natural conditions the surface of a soil is commmonly subjected to substantial variations in temperature, moisture content, and relative humidity. The use of short time periods for equilibration is dictated by the need to minimize complications arising from hydrolysis, microbial decomposition, volatilization, and other factors. Although published data suggest that later stages of sorption reactions continue over weeks or months, there is a lack of quantitative data regarding these long-term sorption phenomena.

From the standpoint of the long-term behavior of toxic chemicals in soils and sediments, desorption studies are also of critical importance. Desorption generally appears to differ from sorption, particularly with respect to reaction rate. Desorption reactions may be responsible for the fact that it is generally more difficult to extract an "aged" soil residue than it is a freshly incorporated soil. Therefore, a better understanding is needed of the effects of time, cyclic variations in temperature and moisture content over time on the sorption and desorption of toxic chemicals on soils and soil constituents.

The liquid/solid ratios employed during sorption tests is a related area of investigation requiring further pursuit with respect to testing methodologies and the validity of obtained data. Because of the markedly different character of these systems, especially with respect to the concentrations of contaminants, oxidation-reduction conditions must be considered in designing sorption and leaching tests for materials in landfills and concentrated sediment systems such as those associated with dredged sediment disposal (Weber et al. 1976; Lee 1978). These systems are generally anoxic, which tends to promote the release of many contaminants (Weber et al. 1976). However, with few exceptions, the concentration of contaminants in the anoxic leachate is a poor measure of the potential impact of the leachate on environmental quality. Eventually these leachates will come in contact with dissolved oxygen, which will result in removal of many contaminants through sorption on iron hydroxide floc. Accurate assessments of the release of contaminants from landfills and from sediments dispersed in natural waters require better understanding of the role of oxidation-reduction reactions in influencing sorption/desorption reactions.

Conventional sorption studies generally involve analysis of the equilibrium concentration of a compound remaining in solution. A better understanding of sorption processes on soils and sediments may also result from examination of that portion of the compound that has reacted with the soil or sediment surface. Information on any changes in compound speciation and/or character resulting from interaction with the surface of a soil or sediment is required to provide a better basis for estimation of hydrolysis, degradation, desorption, and other transformation phenomena.

3.3 LEACHING AND EXCHANGE PROCESSES

Consideration of environmental impacts would be relatively straightforward if potentially toxic chemicals were retained in soils and/or sediments at the site of application or deposition. However, the transport of toxic chemicals from points of release, and their subsequent dispersal throughout the various compartments of the environment, result in exposure to both human and other target species.

Exchange processes between soils and sediments and the atmospheric and aquatic compartments of the environment are in large measure determined by such factors as volatilization and sorption/desorption. Additionally, such exchange processes are markedly affected by aerodynamic and hydrodynamic forces operative at the soil-air and sediment-water interfaces. Uptake and release of contaminants by natural water particulate matter is frequently controlled by the hydrodynamic characteristics of both the water and the sediments. Mixing processes within the sediments and between the sediments and overlying waters therefore often govern the environmental significance of sediment-associated contaminants. These mixing processes arise from both physical forces and biological activities (Lee 1970). Further, hydrodynamic factors control the transport of particulate solids and associated pollutants within the water column and into and out of the sediments resulting in differential accumulations of potentially toxic compounds in the environment (Weber et al. 1979b). It is now becoming clear that meaningful modeling of environmental behavior and fate of solids-associated contaminants will require a substantial research effort devoted to characterizing and quantifying mixing and dispersion processes.

Of principal concern are leaching and exchange phenomena affecting migration and movement of potentially toxic chemicals within soils and sediments. Leaching and diffusion of toxic chemicals in soils and sediments represent two of the basic transport mechanisms for dispersal of chemicals within this compartment. In order to evaluate the potential transport of chemicals via these mechanisms, it is necessary to understand the factors which determine the extent of leaching and diffusion. This information is required in making decisions regarding exposure from chemical use and disposal.

The extent to which compounds are leached from soils and sediments is strongly influenced by rates of degradation, sorption, and precipitation reactions. For purposes of this discussion, degradation will be considered negligible. Because leaching is a relatively slow process, only persistent compounds are environmentally significant. While it is recognized that in many situations factors of degradation must be considered, sorption and precipitation reactions mediate the transport of most persistent toxic chemicals and will therefore be considered in greatest detail.

Leaching and diffusion processes are treated separately. In most transport situations one or the other predominates. Leaching is usually the more important transport process in soils when considering how much or how far a compound is moved. One situation in which diffusion becomes significant in soils is in the transport of volatile compounds, such as the diffusion of fumigants through soil or the loss of volatile compounds from soil surfaces.

The relative contributions of leaching and vapor transport can be estimated from solubility and vapor pressure data. Goring (1962) and Helling et al. (1971) have suggested that compounds with water-air ratios (weight/volume basis) under 10^4 will diffuse primarily in air, while those over 3×10^4 will diffuse mainly in water. Using these estimates as a rough approximation, it could be assumed that those compounds predicted to move primarily in the vapor phase would have the potential for rapid transport by a diffusion controlled process. Considerable data are available in the literature on the aqueous solubility of compounds. However, reliable vapor pressure data are obviously lacking, and considerable effort needs to be expended to correct this. These vapor pressure data are similar to those required for evaluating the volatilization potential of compounds.

Much of the literature on predicting transport of toxic chemicals in soils and sediments deals with the transport of organic pesticides in soils (Letey and Farmer 1974; Leistra 1973; and Hamaker 1975), although several reviews discussing some aspects of the transport of heavy metals in soils and sediments are also available (Hutchinson 1975; Fuller 1977).

3.3.1 Leaching

A simple approximate equation for describing the flux, J_s, of a non-interacting or conservative compound through soil or sediment as a function of water flux, J_w, is:

$$J_s = J_w C \qquad (3)$$

where C is the weight-ratio concentration of the compound in the soil water. This equation describes the mass flow of a conservative species, such as the chloride ion, for situations where diffusion and dispersion within the liquid phase are negligible relative to convective transport. A non-interacting species will move with the water front though most chemical species will interact with the soil or sediment and lag behind the water front, depending on the extent of such reactions as sorption or ion exchange. Therefore, characterization of sorption and related processes is most important for prediction of leaching.

Leaching of chemicals through a soil profile is dependent upon the direction and rate of water flow as well as the sorption characteristics of the chemical with the soil. Water flow through soil depends on soil properties and can be quite complex. A number of investigators have examined this subject and, based on their work, several conclusions can be made concerning research needs, particularly in the area of data collection in laboratory column experiments and field studies.

Most leaching models assume a linear isotherm (equation 2) to describe the distribution of a chemical between the solution and the sorbed phases. The linear isotherm is often satisfactory for a relatively narrow concentration range. When dealing with large concentration ranges, as might be the case for many toxic chemicals in the environment, the Freundlich isotherm (equation 1) is more applicable. The sorption of most organics by soils will follow the nonlinear Freundlich isotherm at higher concentration, and serious errors in predicting the extent of leaching can result in such cases if the linear isotherm is assumed. When sorption isotherms are used to improve the predictability of models, it is imperative that sorption phenomena be characterized as to the type of isotherm which best describes a particular system. Although in the modeling process it may be possible to treat most sorptions in terms of a linear isotherm over limited ranges of conditions, it is necessary to know the actual nonlinear relationship in order to properly choose a linear relationship and associated limits of application.

Well-defined isotherm relationships and information relative to the factors and mechanisms influencing sorption reactions are essential for description of the basic processes controlling leaching. Quantitative description of these basic processes must be encouraged if there is any expectation of improving the ability to predict transport. However, immediate data needs for predicting pollutant transport in the natural environment are of necessity somewhat different from those associated with basic research. This difference exists because predictions under natural conditions often require methodologies that have wide application by many people under conditions where variability is uncontrolled. Large errors can be expected under these conditions. Therefore, the predictive tool adopted need only provide rough estimates to be useful in application to the environment.

State-of-the-art methodology does not permit prediction of the precise distribution of a toxic chemical within a soil profile with any success in the natural environment. Long-term estimates of when a material may be expected to appear in the ground-water appear possible, especially if rough estimates can be made for the sorption reactions. Such estimates would describe the arrival time for the bulk of material from a surface event and would assume uniform flow across a field. Certain parts of the drainage would arrive sooner or later than the average due to spatial variation in percolation rates.

The correlations between sorption of un-ionized organic compounds and the organic matter content of soils and sediments is reasonably well established. This class of compounds includes most pesticides and most of the trace organics found in drinking water. From the soil/water distribution, K_d, the soil organic matter/water distribution, Q, is given by

$$Q = 100\ K_d / \%\ \text{soil organic matter} \qquad (4)$$

This correlation is fairly constant from soil to soil for a given chemical. Karickhoff et al. (1979) suggest that for neutral organic molecules the ratio, Q, is related empirically to P - the octanol/water distribution coefficient of the chemical - by:

$$\log Q = (0.52 \pm 0.05) \log P + (0.62 \pm 0.11) \qquad (5)$$

The fraction of chemical in the soil solution can thus be assessed from K_d, P, or Q. The determination of P is a simple laboratory procedure. From a determination of P and the use of equation 5 or a similar equation, a rough estimate of the mobility of neutral molecules in soils is possible. Further investigation into the applicability of such relationships seems warranted since there is already considerable interest in the use of octanol/water ratios for estimating the bioaccumulation potential of organic chemicals.

Laboratory leaching columns and soil thin-layer chromatography (TLC) have both been used successfully to correlate sorption characteristics with the relative mobility of compounds in soils and sediments. The use of soil columns is often preferred because water flow in such systems more closely simulates that in an undisturbed soil or sediment profile. Soil TLC has the advantage of being a more rapid means for determining the relative mobility of a number of compounds in a number of soils and/or sediments. Soil TLC may be extremely useful as a screening tool to determine which compounds might present a leaching hazard and warrant further study with soil leaching columns. Adequate methods are available for the application of either technique. However, there is a need for uniformity of techniques between laboratories using leaching columns as a means to improve predictive capability. Many of the data available in the literature on the leaching of organics in column tests are not comparable because of differences in techniques used by different labs. In addition, investigators often fail to collect all the data, especially water flow characteristics, necessary to evaluate and compare leaching experiments. In a review of 49 commonly used pesticides, no leaching data were found for 27 of the compounds (Farmer 1976). For those compounds for which data were available, the information was difficult to use in predictive evaluations due to lack of uniformity of leaching techniques and soils employed by the different investigators.

The modeling of pollutant transport due to leaching in laboratory columns has been fairly successful. Using sorption and water flow characteristics the distribution of chemicals within a soil profile in the laboratory can be simulated relatively well. Problems can be expected when these models are applied to the field. Spatial variability is likely to be a serious problem in simulation of field events.

Laboratory modeling has looked at sorption and the exclusion volume (dead-end pores) concept to simulate laboratory columns. These usually assume a diffusion process mediating the compound in solution in the stagnant phase entering the convection stream. In these models sorption processes are usually linearized to give

$$\beta S = R \, \Theta \, C \qquad (6)$$

where R is the sorption coefficient, K_d, expressed on a soil volume basis; S and C are the sorbed and solution concentrations (equation 2); Θ is the volumetric water content in cm^3/cm^3; and β, the soil density in g/cm^3, are included to convert to a soil volume basis. It can be shown that transport by leaching will be reduced by the factor $1/(1 + R)$ with respect to mobile ions. A rough estimate of the depth of maximum pentration of a compound can be obtained by dividing the depth of penetration of the water front by $(1 + R)$.

One problem that is only beginning to be approached by investigators is the influence of wetting-drying cycles on the upward mobility of chemicals after they have entered the soil profile. The ability to predict upward mobility is essential for predicting the runoff and volatilization of soil-incorporated water-soluble compounds from the soil surface. This is a complex problem involving water flow and water evaporation to and from the soil surface. Several models describing chemical runoff from non-point sources for humid regions of the U.S. are available (Hutchinson 1975; Donigian and Crawford 1976; Stewart 1976; and Wauchope 1978). There is a need for field testing and verification of existing chemical runoff models, and for expansion of such models to include more arid regions of the U.S.

The methodology for field investigations of leaching in soils has not progressed sufficiently to permit recommendation of a definitive procedure. As with laboratory columns there is a lack of uniformity in procedures and often a deficiency of data collection on water flow characteristics. The problem is exaggerated in field experiments because of the natural variability involved when working with soils in their undisturbed (native) state.

It is important that field investigations be continued. They are necessary to verify the models developed with laboratory leaching columns. Though unlikely there will be much success in predicting the absolute distribution of a chemical from a soil profile in the field, there is the possibility of estimating the depth of maximum penetration or finding a range of expected concentrations at expected depths.

Current leaching studies with soils are characteristically performed with distilled water or water of low ionic strength to simulate irrigation water. The application of current leaching information to the problem of landfill leaching is probably not justified. Leachate from land disposal practices can be expected to contain high concentrations of soluble organics and inorganics which may interfere and/or compete with each other for sorption sites. The effects of concentration parameters on leaching are largely unknown and require further investigation. A likely result of competitive forces on sorption is increased leaching and analytical procedures are expected to be more complicated with land disposal leachates.

Studies on metals over the past decades have provided sufficient data to predict short-term consequences of metal contaminations of agricultural soils. Most knowledgeable researchers in the field are of the opinion that phytotoxicities and quantities of metals sorbed can be assessed accurately where metals are applied to soils in the form of wastes for periods up to a decade. The longer-term consequences of metals added to soils, as well as predictions of what occurs when the metal additions cease, are more uncertain. A basic understanding of the chemistry of the metals in soils is required for prediction of long-term consequences as well as of the ultimate fate of metals added to soils in the form of waste. Factors controlling the solubilities and the nature and rate of chemical and microbial transformations need to be delineated. Factors which control the availability of metals to plants are also not well established. These are dependent upon chemical forms present, soils and sediments, and upon competitive interactions. A thorough knowledge of the chemistry of metals in soils and sediments should facilitate the required long-term predictions.

Release or mobilization of metals from soils and sediments by the action of added complexing agents is a substantial concern. Similarly, the role of metal speciation on the removal of metals from solution onto soils and sediments is of importance in regulation of metal transport. At present, little information other than total metal uptake and release is available. Different types of sites in soils and sediments have different affinities and strengths of binding for heavy metals. Lack of consideration of speciation with respect to extent and strength of uptake, or release of metals from the solids as a consequence of the addition of complexing agents, precludes use of such information except for the given conditions of testing.

Research should be conducted to establish which phases of sediments and soils are active in metal uptake, and whether binding strength is similar among various soils and sediments. Information regarding the ability of complexing agents to release metals from metal-amended and unamended soils and sediments is required. This research should consider release from each of the several metal phases present. The degree to which metal release capability is constant between the same phase of various soils and sediments should be ascertained.

3.3.2 Diffusion

Non-vapor diffusion in soil is not likely to be a predominant transport mechanism so this discussion will be limited to vapor diffusion. If reliable vapor density-temperature data are available for a compound, it should be possible to develop models for successfully predicting gaseous flux.

A gas flow model has been applied to the landfill disposal of wastes containing volatile components by Farmer et al. (1978). A possible avenue for the escape or migration of a pollutant from a landfill is via volatilization through the soil cover. The assumption can be made that the compound is nearly insoluble in water so that diffusion in the vapor phase in the soil pores is the only mechanism by which it can move through the soil cover. Such an assumption is valid for certain compounds, such as certain chlorinated hydrocarbons for which diffusion is controlled by the air-filled porosity of the soil. The limiting step for volatilization is the rate at which the compound diffuses through the soil cover to the surface. Farmer et al. (1978) suggest that for any particular land disposal situation, the volatilization flux will be determined by the soil air-filled porosity and depth of the soil cover, both of which can be managed by the landfill designer to meet existing regulations for vapor emissions.

If cracks or other small openings develop in the soil cover an appreciable increase in flux through the cover will result. The practice of placing toxic waste with materials such as municipal solid waste, which is subject to settlement, could cause such cracking and increase flux.

Another consideration to be given to the use of land disposal for volatile toxic chemicals is the need for long-term arrangements for ensuring the integrity of soil covers. Some compounds that pose a volatilization potential from land disposal will also be resistant to degradation. Assuming no degradation, calculations for hexachlorobenzene indicate that it can continue to volatilize at maximum rate for several centuries when placed on land. The integrity of the soil cover must be maintained for this period by preventing such disruptions as erosion or digging.

In the course of investigations into the land disposal of volatile wastes Farmer et al. (1978) found that some wastes contained a dense organic liquid in which hexachlorobenzene is highly soluble (23,000 µg/ml) Thus, organic solvents as well as water must be considered as the carrier in mass flow.

A variety of forces have been identified as significant factors operative in the exchange of toxic substances between sediments and water. A clear need exits for research directed toward quantification of the relative influences of physical disruption or mixing (turbulence, gas movement), biological mixing (bioturbation) and diffusive transport factors in different sediment and water environments.

3.4 PHOTODEGRADATION AND VOLATILIZATION

3.4.1 Photodegradation

Absorption of light by a chemical is absolutely required for direct photochemical reaction. However, the molecule of interest does not itself have to absorb light energy if other molecules, so-called photosensitizers, are available to participate in the primary photochemical event. Once a photosensitizer molecule has been promoted to an excited state it can transfer its energy either directly or indirectly to the molecule of interest which, once excited, can dissipate its energy by several mechanisms including the breaking of formation of chemical bonds.

Environmental photodegradation occurs exclusively through the interaction of sunlight with molecules. Photodegradation experiments performed in the laboratory have frequently relied on artificial light due to the variable and often unpredictable quality and quantity of sunlight available over any given period of time. The high energy end of the sunlight spectrum that reaches Earth (290 to 400 nm) can be duplicated in the laboratory through use of such sources as mercury arc lamps (Zepp et al. 1975), conventional fluorescent lamps with borosilicate glass filters (Crosby and Moilanen 1973) and xenon arc lamps (Lockhardt and Blakely 1975).

Knowledge concerning the photochemical fate of synthetic chemicals purposefully applied to land (eg., pesticides, waste effluent resulting from more stringent water quality standards, municipal and industrial solid wastes, etc.,) will increase in importance in the next few years. Therefore, an important transition must be made between the laboratory and the real environment to identify and understand those factors in the environment which modify the results of laboratory photodegradation experiments.

Photochemical reaction of chemicals in soils and on sediments does not occur throughout the various soil and sediment layers but only at the surface (Crosby 1972). Some researchers have tried to duplicate the soil environment in the laboratory. Hautala (1976) has examined the photochemical decomposition of 2,4-D, sevin, and parathion on three types of arable soils. His experiments determined that moisture content of the soils was a critical factor as was the type of soil used and the presence or absence of a detergent. For example, anionic surfactant decreased the extent of photolysis of 2,4-D on dry or saturated soils. In the presence of excess water ("wet" soils), detergent dramatically increased the rate of photolysis.

Carey et al. (1976), in an effort to simulate the interactions between PCB's and suspended sediments, studied their photodechlorination in the presence of TiO_2. Based on their results, PCB photolysis in the presence of suspended solids does not proceed along the same pathway as in the absence of such sediments.

Spencer et al. (1978) have used a thin layer of soil dust in the laboratory to simulate the upper soil layer for studies of parathion photodegradation. Smith et al. (1978) have also performed laboratory photodegradation studies using a thin-layer soil technique.

Based on these works and on reviews of the subject by Crosby (1972) and Plimmer (1972), it can be concluded that the phototransformation of certain synthetic chemicals may be an important way in which these chemicals are altered in the environment. Only very limited field work on chemical photodegradation in the environment has been performed so a number of important questions remain unanswered. Since a large group of new compounds may be either directly placed on the land or discharged to the land after use, there remain many undocumented areas regarding their photodegradability.

The circumstances under which photoreaction of materials on soils and sediments may be important should be researched, and the physicochemical properties or structure-activity relationships which would predict phototransformation of one compound on various types of soils should be explored. More information is needed about which properties to consider when predicting photodegradability of land-applied materials not in direct contact with soils and sediments, as well as the soil and sediment characteristics and parameters which determine routes and rates for photochemical reactions of specific compounds. Laboratory procedures for photodegradation should be identified and field tests made to verify any laboratory models. The importance of phototransformation of chemicals on airborne particulate matter or in the vapor phase following volatilization from soil or sediment should be considered. Finally, a check should be made to see if there are laboratory screening tests based on results of experiments designed to answer questions in the aforementioned areas to allow relatively rapid and predictive photodegradation experiments on a large number of compounds.

3.4.2 Volatilization

Organic pollutants principally enter the atmosphere by volatilization, by direct injection such as pesticide sprays or stacks from industrial plants, and by movement of wind-blown dust particles (Spencer et al. 1973). The soil becomes both sink and source for a large portion of the chemicals that enter the environment by intentional application to the land, inadvertent spillage, or release into the air. One of the management tools required for the utilization of land as a waste disposal medium is the ability to control volatilization of the chemicals in the waste, whether in landfill or mixed into the soil after application.

Post-application volatilization of pesticides under field conditions was thoroughly reviewed by Taylor (1978) and will not be repeated here. The reader is also referred to other reviews on pesticide volatilization by Hamaker and Thompson (1972), Spencer et al. (1973), Wheatley (1973), Guenzi and Beard (1974), and Plimmer (1976).

Potential volatility of a chemical is related to its inherent vapor pressure; however, actual vaporization rates will depend on environmental conditions and other factors that modify or attenuate the effective vapor pressure or behavior of the chemical at a solid-air or liquid-air interface. Vaporization from surface deposits depends only on the vapor pressure of the chemical and its rate of movement away from the evaporating surface. Vaporization from aqueous systems depends on the vapor pressure of the chemical and its water solubility. Vaporization from soil is controlled by solubility and sorption as well as vapor pressure. Consequently, no single physicochemical property is adequate to describe and predict the probable vapor behavior and fate of a chemical in the environment or its likely method of transport in the atmosphere. However, estimates of relative vaporization rates useful for environmental indices can be calculated from basic physical properties of vapor pressure, water solubility, sorption, and persistence if reliable values for each are known at various temperatures.

The vapor pressures of many organic chemicals of environmental interest increase aproximately 3 to 4 times for each 10°C increase in temperature. Consequently, reliable values for vapor pressures at various temperatures are necessary to estimate vapor losses of the chemical from surface deposits, to predict partitioning between water and air, and soil, water, and air relative to volatility from water solutions and from wet soils, and to calculate residence times in the atmosphere of chemicals in droplets and aerosols.

A search of available literature on the vapor pressure of 49 commonly used pesticides revealed both a lack of vapor pressure data for many of the pesticides and a wide variability in vapor pressure of the same compound reported by different authors (Spencer 1976). The inconsistency in reported vapor pressure values attests to the need for accurately determining vapor pressures of pesticides and other toxic organic chemicals by a standard procedure, preferably one which relies analytically upon a specific method for determining the chemical of interest.

The gas saturation method has proven to be a reliable method of measuring vapor pressures of pesticides (Spencer and Cliath 1969; Spencer et al. 1978; U. S. Environmental Protection Agency 1975) and should be equally reliable for determining vapor pressures of other toxic organic chemicals with vapor pressures in the range of those exhibited by most pesticides. When this method was recently used to measure the vapor pressure of technical grade and purified ethyl and methyl parathion, no significant differences in vapor pressure were observed between technical grade or purified materials of either chemical (Spencer et al. 1978). The observed vapor pressures, which indicated methyl parathion is approximately twice as volatile as ethyl parathion, are consistent with their relative persistence on foliage as reported by Ware et al. (1972, 1974). In contrast, the most frequently quoted literature value for vapor pressure of parathion (Bright et al. 1950) is approximately four times higher than the reported vapor pressure of methyl parathion (Guckel et al. 1973).

The relationship between vapor loss rate and vapor pressure by measurements of vapor loss rates from various surfaces types under the same conditions is helpful in comparing relative volatility of potentially toxic chemicals. This measurement can be accomplished by a procedure such as that described by Spencer et al. (1978) or by Guckel et al. (1973).

Incorporation of an organic chemical into the soil decreases the concentration at the evaporating surface thereby greatly reducing the volatilization rate. When a chemical is mixed into the soil loss by volatilization involves desorption of the chemical from the soil, upward movement to the soil surface, and vaporization into the atmosphere. Consequently, the volatilization loss rate of a chemical in soil will be related to the vapor pressure of the chemical within the soil and its rate of movement to the evaporating surface. The rate of loss initially will be a function of the vapor pressure of the chemical as modified by sorptive interactions with the soil surface. Volatilization rate decreases rapidly as the concentration at the surface of the soil is depleted, and the rate soon becomes dependent upon rate of movement of chemical to the soil surface (Spencer, Farmer and Cliath 1973; Farmer et al. 1972, 1973). The two general mechanisms whereby pesticides move to the evaporating surface are diffusion and mass flow in evaporating water. Usually both mechanisms operate together in the field where water and the chemical vaporize at the same time unless the chemical is essentially insoluble in water or has a sufficiently high vapor pressure to result primarily in vapor phase movement through the soil pores rather than movement within the soil solution.

In the absence of evaporating water volatilization rate depends upon rate of movement of the chemical to the soil surface by diffusion. If diffusion coefficients for the chemicals in the soil are known, diffusion equations can be used to predict changes in concentration of the chemical within the soil and its loss rate at the soil surface. Mayer et al. (1974) and Farmer and Letey (1974) have obtained good agreement between volatilization rates predicted from mathematical models using diffusion coefficients and volatilization rates observed in the absence of evaporating water. Diffusion processes in the soil will also control volatilization losses of chemicals in the presence of evaporating water if the chemical does not move significantly by mass transfer with the water due to its insolubility or to its much greater mobility in the vapor rather than in the liquid phase of the soil system (Farmer et al. 1978).

In addition to factors directly affecting vapor behavior, the proportion of the total amount of the chemical in the soil lost to the atmosphere will depend upon the resistance of the chemical to degradation and leaching in the soil. Any models for predicting vapor behavior must take into account the relative degradation rate of the chemical compared with its movement into the atmosphere. With methyl parathion (Spencer et al. 1978) and parathion (Yang 1974) biological degradation in the soil, rather than volatilization, is the major pathway for dissipation from soil. The total methyl parathion volatilized over a 33-day period when added at 10 ppm to Flanagan silt loam averaged only 0.25 percent of the amounts incorporated into the soil, but after 33 days only 0.5 percent of the added methyl parathion remained in the soil. This is in direct contrast with lindane for which much higher volatilization rates were observed even though the vapor pressure of lindane is somewhat lower than that of methyl parathion; its greater persistence results in much greater losses by volatilization.

Many industrial wastes are disposed of in landfills. These wastes may or may not be subsequently covered with a layer of soil to prevent or reduce vapor loss of any potentially toxic organic chemicals. Volatilization of the chemicals from uncovered wastes will follow the principles of vapor loss from inert surfaces, and the actual rate of loss will depend upon weather variables affecting vapor pressure and air turbulence at the waste site. Vapor loss of chemicals from a landfill in which the waste is covered with a layer of soil will be at a greatly reduced rate in accordance with the above principles on vapor loss from soil. Volatilization losses will be related to the rate of movement of the chemical through the soil cover into the atmosphere.

Soil cover provides an efficient means of decreasing the loss of volatile chemicals placed in a landfill (Farmer et al. 1976). One of the management tools required for utilization of landfill as a waste disposal site is an ability to control the volatilization of hazardous chemicals from the wastes. Farmer et al. (1976, 1978) recently completed a study designed to gather data useful to the landfill planner in controlling vapor movement of hexachlorobenzene by utilizing a soil cover to limit vapor loss to the surrounding atmosphere to an acceptable level.

Hexachlorobenzene (HCB) is a persistent, water-insoluble, fat-soluble organic compound. Farmer et al. (1976, 1978) used a simulated landfill to determine the parameters necessary to predict volatilization of this compound from wastes placed under a soil cover. Covering the wastes with only 1.0 cm of soil reduces vapor flux of HCB from 363 to 5 ng/cm^2/hr, or by 98.6 percent, indicating that soil is a very effective covering material. They found that soil depth and soil air-filled porosity were the two prime factors controlling movement of the vapor in soil.

The relationship between vapor flux, soil depth, and air-filled porosity is predictable on the basis of known factors controlling vapor behavior in soil. Since HCB is essentially insoluble in water, mass flow in the evaporating water will not be important in moving this compound to the soil surface; consequently, diffusion in soil pores will be the only mechanism available. Because of the water-air partition ratio of compounds such as HCB, and the higher rate of diffusion in air than in water, diffusion of these compounds will be primarily in the vapor phase through the soil pores. Thus, vapor loss can be considered as a diffusion controlled process involving only vapor phase diffusion through air-filled soil pores.

Since soil porosity is controlled mainly by soil compaction and soil water content, vapor flux can be decreased by increasing compaction and increasing soil-water content as well as by increasing soil depth. Vapor flux of HCB through a soil cover of 30 cm or greater would be less than 1 $ng/cm^2/hr$ (1 kg/ha/year) compared with a vapor flux of 363 $ng/cm^2/hr$ from the uncovered waste under the same conditions. For compounds such as HCB, increasing soil-water content greatly decreases vapor loss rate by decreasing vapor phase diffusion through the soil due to its effect on air-filled porosity. For compounds which are more water soluble, soil-water content may have varying effects and may increase or decrease vapor loss depending upon the potential for downward or upward movement of the chemical in the water phase.

There is a definite need to develop and test models for predicting volatilization of various organic chemicals from the soil. These models should include simultaneous movement of the chemical toward the surface by diffusion and mass flow in the evaporating water, while also considering changes in concentration from degradation of the chemical in the soil.

A second serious gap in the knowledge of vapor behavior concerns the extrapolation of laboratory data on relative volatilization rates to field situations. Volatilization models developed from physicochemical parameters and controlled vapor loss studies in the laboratory should be calibrated with field measurements of volatilization rates with the chemical under study applied to the soil surface and incorporated within the soil to test predictive capabilities.

Vaporization from water-containing sediments or water-sediment systems should be governed by the same factors affecting vapor losses from water after considering the reduction in concentration of the chemical due to sorption on the sediment.

Success in predicting vapor loss rates with any model depends upon the availability of reliable values for vapor pressures, water solubility, sorption characteristic, and persistence or degradability of the chemical in the environmental system whether it be soil, water, or sediment. A need exists for collection of basic information on chemicals to be studied utilizing standard procedures so that data gathered by different investigators can be utilized with confidence.

It is impossible for all new chemicals to initially be examined in detail for screening purposes. Applying the baseline data on the dynamics of representative compounds will be more practical in providing comparative data on the photodecomposition and volatilization of the new chemical. These comparative data could become much more useful if a set of reference, or so-called "benchmark," chemicals were established with representative properties.

Reference compounds can be chosen from the most widely used compounds for which models could be validated against results obtained in field studies and model ecosystems.

Selection of benchmark compounds should be based on classes of chemicals and their widespread uses. Subdivision of the classes may become necessary where widely differing octanol/water partition coefficients or other sorption parameters are found within one class. The physical and chemical constants for reference compounds should be examined including vapor pressure, hydrolysis rate as a function of pH, water/octanol partition coefficient, quantum yield for photolysis, solubility, etc. These criteria can be used to identify the situation most likely to promote photodegradation or volatilization. The chemical behavior of the benchmark compounds should be determined in a set of well defined natural systems chosen to represent as wide a range of environments as possible. Benchmark data should be incorporated into simulations of the expected dynamic behavior of the chemicals and validated against suitable field data. Other chemicals relative to the benchmark compounds should be assessed by lifetime/concentration measurements for free and sorbed chemicals and active metabolites in the critical test systems. Associated chemical and physical data can be assembled and used to predict behavior to provide simulations of photodecomposition or volatilization patterns which can be examined in the light of results obtained in test systems and to delineate the limitations of these simulations.

As the library of chemodynamic information grows and the models are refined, deviations of new compounds from predicted behavior will be readily apparent. Deviations of new compounds from predicted behavior should be examined closely since they may indicate where further research is needed in assessing the behavior of new chemicals.

3.5 PHYSICOCHEMICAL AND BIOCHEMICAL TRANSFORMATIONS

Synthetic chemicals introduced, deliberately or inadertently, into soils or sediments may be subjected to one or more kinds of transformation. Many toxicants are volatilized and lost from the site. A large number of organic compounds are subjected to nonbiologically effected chemical changes; such nonbiological alterations in structure are characteristic of many classes of simple molecules. Other organic substances that are present at the very surface of soils undergo relatively common photochemical changes. In addition, organic and inorganic chemicals can be acted upon biologically with biological or enzymatic reactions bringing about changes in the structure of synthetic molecules. These biotransformations have been noted in diverse soils and sediments.

The agents responsible for major biologically induced changes on soils and sediments are usually bacteria or fungi microorganisms. The microflora stand out in the biological realm because of their role in the degradation of synthetic chemicals, including most of the major changes that are deemed to be of ecological and human health significance in these environments. Although abiotic processes are extremely significant in transforming synthetic toxicants, the chief (and often the sole) means by which these compounds are transformed to inorganic products is a result of microbial activity in aquatic and terrestrial environments. There are few documented instances where an organic chemical, particularly one of some degree of complexity, is completely converted abiotically to an inorganic product. Microbial inhabitants appear to be the chief agents for complete destruction of such chemicals though fires may also lead to complete destruction. Mineralization is the term used to designate the total destruction of an organic compound and its conversion to carbon dioxide and other inorganic products. Mineralization is a characteristic of microorganisms and is rarely noted in abiotic transformations. Conversely, some inorganic pollutants are converted into persistent organic compounds by microbiotic action in soils and sediments.

Many synthetic organic compounds which are not mineralized or transformed accumulate in the environment. These persistent molecules may be hazardous to humans, domestic animals, or wildlife (DDT and PCB's), create nuisance problems because of the odor or taste they impart to waters (chlorophenols), cause serious injury to crops grown in rotation (triazine herbicides), increase the cost of municipal waste disposal (the synthetic polymers making up a significant portion of the solid waste of cities), or their influence may largely be associated with aesthetic deteriorization (plastic containers in the countryside or some surfactants in waters). The susceptibility to biological and chemical transformation of each organic compound entering soils and sediments must be determined in order to discover which chemicals accumulate in soil and sediments creating potentially hazardous environmental situations.

Incomplete degradations, caused by biological or abiotic means, are often of great practical concern. The products of these incomplete reactions may have greater toxicity than the parent molecules, exhibit toxicity to organisms different from those affected by the original substance, show greater persistence in soils and sediments than the parent chemical, or may be subject to bioaccumulation greater than that of the parent molecule. In addition, the toxicological art is constantly growing and a product that today is deemed to have no toxicological significance may subsequently be revealed to harm one or more species. As a result, the incomplete breakdown of chemicals that is characteristic of abiotic as well as many microbial processes is of great practical concern. The mineralization of organic compounds must be established. Simple and inexpensive test procedures are adequate for assessment of mineralization though the existing techniques must be validated.

Classically, three general sources of biomass have been used for laboratory biotransformation studies. One of these classes, a microbiologically pure culture, is used in the study of biotransformations of an individual compound by one species of microorganism. Pure culture studies are attractive from a microbiological standpoint, but the relevance of the results of such studies is not always evident. Enrichment cultures of microorganisms derived from soils, waters, or sludges have also been used. Studies performed with enrichment cultures are often difficult to reproduce because of microbiological variability but are attractive because of the environmental relevance of the original biomass source. The use of artificically mixed cultures (i.e., combinations of several pure cultures) is less attractive than the other biomass sources because data from studies performed are neither easily explained microbiologically nor are they environmentally relevant.

Some chemicals considered nonhazardous at environmental concentrations may in fact be converted to highly toxic chemicals. For example, dialkylamines and nitrate at environmental concentrations rarely are problems, but microbial and/or chemical reactions in waters, and soils lead to the formation of carcinogenic nitrosamines from these precursors (Ayanaba et al. 1973; Ayanaba and Alexander 1974). Further, an innocuous precursor may disappear readily but convert to a persistent and possibly toxic product. These considerations suggest that major research is needed on the products of biological and abiotic transformation of synthetic chemicals in soils and sediments. The need for identification should be tempered by the available toxicological information.

The transformation of products from nontoxic to toxic forms is evident in the conversion of the fungicide thiram to a carcinogenic nitrosamine (Ayanaba et al. 1973) and the conversion of the antifungal pentachlorobenzyl alcohol to phytotoxic chlorinated benzonic acids (Ishida 1972). The need for such research is reinforced by observations of the conversion of a chemical retained on sediments or soil surfaces into a product which is taken up in biological food chains, such as the methylation of mercuric ions so that the mercury retained by cation exchange on colloidal surfaces is available for uptake into animal tissues (Wood 1971). Few of the products formed from the chemicals that are released into waters and soils have been identified, and the few established products are typically those derived from the microbial or abiotic transformation of pesticides. Chemicals that originate in industrial or domestic operations have received essentially no attention.

It is important to determine whether particular synthetic organic compounds are acted upon by biotic or abiotic mechanisms to understand the kinetics of the process, possible products, and information on the likelihood of formation of polymeric, complexed or "bound" residues of the chemical. Microorganisms may use an organic molecule as a nutrient and convert much of the carbon in the chemical to carbon dioxide, provided oxygen is available. Simultaneously, the organism will assimilate some of the carbon in the molecule into microbial cells. With information that microorganisms are responsible for a process, the carbon not accounted for as carbon dioxide or known products can frequently be ascribed to the formation of biomass which is of no toxicological significance. If the mechanism is abiotic, no cellular constituents are generated and additional chemical information is required. Further, knowledge that microorganisms are responsible for transformation will aid in kinetic investigations in so far as the rates of bacterial processes parallel the logarithmic growth of these microorganisms, at least under ideal circumstances.

Relatively little is known about the role of soil- and sediment-dwelling macroinvertebrates in directly causing transformations of synthetic chemicals or indirectly affecting these processes as they influence the microbiota that carries out the transformation. In addition to whatever role these invertebrates might play in mechanically transporting materials on or within soils and sediments, research is required to determine the role of these invertebrates in transforming synthetic chemicals, either directly or indirectly. Attention might be given to their role in the transfer and transformation of litter and detritus, and in reduction of particle sizes to facilitate microbial action.

Knowledge that a chemical is transformed in soils and sediments is not sufficient for regulatory action. Research is needed to establish the types of kinetics and kinetic expressions of biological and abiotic transformations to allow meaningful predictions of the environmental behavior of chemicals.

Field evidence shows that chemicals which are destroyed rapidly in one environment are largely or wholly resistant in other environments. This is evident in the longevity of polysaccharides and other natural polymers in peat as long as the peat remains under water; once the area is drained the polymers are readily converted to carbon dioxide and other simple products. Similarly, hydrocarbons endure in nature in anaerobic regions but they are often quickly destroyed in aerobic environments (Alexander 1973). The effects of environmental factors on biological and abiotic transformations in natural environments should be explored. Although considerable attention has been given to temperature and pH, the significance of surfaces in sorbing or complexing toxic chemicals, the importance of anaerobiosis, the effects of chemical mixtures, and the role of plants require further characterization.

Sorption of synthetic chemicals to colloids in soils and sediments as protection against biodegradation requires attention. Such sorption frequently increased the resistance of organic compounds to attack. For example, proteins bound to clays are frequently depolymerized by enzymes far more slowly than the same protein found in solution (Esterman et al. 1959). Similarly, the complexing of a normally degradable substance may render it refractory to microbial attack. Polysaccarides are less available to enzymatic degradation by microorganisms when they are bound to polyaromatics of environmental importance than when they are free of the binding agent. In addition to surface adsorption, clay minerals may entrap organic substances within their lattice structures and account for the occasional resistance of chemicals that are usually quickly destroyed.

The role of one chemical or a mixture of chemicals in affecting the transformation of specific compounds of interest requires definition. Few studies have been concerned with the interaction of chemicals as they affect transformation reactions in nature. Thus, one chemical may be used by the active population, and these microorganisms may then not transform the primary chemical of concern, although they would have done so in the absence of the second compound. Conversely, if co-metabolism is important, refractory organic compounds might be co-metabolized more readily if the environment is rich in readily biodegradable compounds that support microbial proliferation.

The significance and means of enhancing co-metabolism should be established. Co-metabolism refers to the metabolism by a microbial population of a chemical it cannot use as a nutrient source. A compound acted upon in this manner, though transformed biologically, will not be converted to microbial cell constituents and therefore the kinetics of the transformation will not parallel microbial growth inasmuch as the population is not increasing in response to addition of the chemical to water or soil. Furthermore, chemicals undergoing co-metabolism are not mineralized (Alexander 1979). Hence, products derived from the parent molecule will be likely to occur. The small amount of existing knowledge of co-metabolism suggests that the parent toxicant is not significantly modified enzymatically and it is likely that the products are themselves toxic. Surprisingly few data are available on the precise role of co-metabolism in natural environments, but the foregoing considerations suggest that additional attention ought to be paid to this phenomenon.

Should the chemical be acted upon largely or solely by biological mechanisms, the lack of increase in microbial numbers or biomass, as is typical of co-metabolism, will be reflected in a prolonged persistance of the toxicant provided that the responsible microbial population is initially small. It is possible that co-metabolism can be enhanced by stimulating the growth of the responsible population. Such stimulation would require the addition of organic nutrients other than the toxicant, and the possibility of this type of environmental manipulation to enhance the destruction of toxicants should be explored. In addition, the kinetics of co-metabolic processes in nature have not received attention. Since this phenomenon appears to be wide and significant, the kinetics need to be delineated.

When measuring the biodegradability of particular compounds for regulatory, developmental, or research purposes, a simple model of a natural ecosystem is employed in order to maximize convenience and minimize expense. Typically, one or very few concentrations of the test chemical are used and characteristically the level of the chemical in the laboratory model is much higher than found in nature. However, Michaelis-Menten kinetics suggest that the rate in nature would be lower than in the laboratory. The reduction in rate may be directly proportional to the lowered concentration of the chemical (as suggested by the linear portion of the Michaelis-Menten plot), but the concentrations equivalent to the linear portion of the plot are unknown for nearly all synthetic chemicals entering soils and sediments. Moreover, some evidence now exists that there is a threshold for biodegradation below which there is no microbial destruction (Boethling and Alexander 1979). Alternatively, the concentration in the laboratory tests may be high enough to inhibit microbial transformation that would otherwise occur at the low concentrations in nature. Thus, a chemical in the laboratory model either would be decomposed at a greater (or sometimes lesser) rate than at the lower concentration in nature, or it may be decomposed in the laboratory model but not at all in soils and sediments. Hence, the influence of chemical concentration on the rate of its biological transformation in natural environments needs to be determined.

Alternate enzyme substrates in waters or soils or the presence of surfaces upon which a synthetic chemical can be concentrated may alter the apparent concentration dependence of rates of biological transformation so the effect of additional chemicals and surfaces in regulating the rates in nature must be evaluated. Plausible microbiological explanations can be advanced to explain the concentration dependence of biodegradation and the presence of a threshold concentration below which microbial attack does not take place, but these hypotheses have not been tested under laboratory conditions simulating natural environments. The effect of inoculum size on rates of microbial transformations in laboratory tests must also be evaluated.

Organic compounds as well as potentially toxic inorganic chemicals are assimilated from soil by plants. These chemicals may affect animals feeding on the plants and thus be important to herbivores or grazers as well as to other organisms in food chains. If the toxicants enter food crops, they may affect humans. Except for pesticides and heavy metals little attention has been given to the uptake of toxic molecules by higher plants. Research on those toxics relative to food chains is of great importance and should consider factors (including soil type) affecting assimilation by plants and animals or classes of molecules involved.

Many toxicants as well as other organic compounds are resistant to destruction or appreciable modification in natural environments. The list of resistant molecules is long but as yet incomplete. These chemicals are employed for many purposes and the significance to man, wildlife, and natural ecosystems may sometimes be appreciable. The reasons that certain organic compounds are resistant in all environments (that is, are intrinsically resistant to degradation) and the reasons others persist in one environment but are destroyed in another must be established. Some speculation on the basis for resistance of recalcitrant molecules to microbial attack exists, but few of the hypotheses have been tested.

An extremely limited number of correlations between chemical structure and microbial transformations in soils and sediments have been made (Alexander 1973). It is essential to determine what structural characteristics are correlated with, or account for, resistance to microbial mineralization or co-metabolism. This type of information should permit regulatory agencies to determine the chemicals that are more likely to be environmental problems because of their persistence and availability for biomagnification. The information will also be of use to industry as it seeks new chemicals that will not endure in waters and soils. The few generalizations that exist in this area relate to a limited number of surfactants, insecticides, herbicides, model aromatic compounds, and aliphatic acids. From the very few investigations in this field, it appears that slight changes in the structure of many molecules appreciably alter the rate of their destruction in natural environments. These changes allow a molecule which previously was not able to support microbial growth to be co-metabolized into one which is readily decomposed.

With regard to the recommendations above, generalizations must be provided on classes of molecules which are susceptible to mineralization or co-metabolism and the effect of concentration, aeration, or surfaces as well as other environmental factors on biodegradation of classes of chemicals. In the absence of such generalizations each one of the vast number of compounds of concern to EPA (and regulations for TSCA) would have to be evaluated separately. These generalizations should ease the task of regulatory agencies and private industries in determining whether particular compounds or classes of compounds pose environmental problems, and the information should facilitate identification of those organic molecules which may be serious environmental pollutants.

3.6 CHARACTERIZATION OF SOILS AND SEDIMENTS

As discussed in preceding paragraphs, the fate of potentially toxic substances in soil systems is dependent on a variety of factors, including but not limited to: sorption-desorption phenomena, leaching and diffusion phenomena, chemical and biochemical transformation, photodegradation, and volatilization. The magnitude and nature of the effects of the last four factors are largely influenced by the nature and extent of sorption-desorption reactions. These reactions are in turn regulated by the physical and chemical nature of the sorbent. Section 3.6 identifies major properties of soils and sediments which are of importance relative to the sorption-desorption of chemicals and characterization of the leaching, diffusion, and environmental fate of these chemicals.

Aquatic sediments are similar in some respects to terrestrial soils. Erosion of soils is a major source of sediments. It should follow that sediments would be similar in many aspects to the soils from which they derive and this is the case in some instances. Erosion is a size-selective process; smaller particles are most vulnerable to erosion. Frink (1969) found that the clay content of a lake sediment was fivefold greater than that of the upland soils, while the sand content was substantially reduced. The most obvious difference between soils and sediments is perhaps the most important: soils are only periodically exposed to a mobile water phase; the extent of hydration of the soil particles diminishes over the prolonged periods during which they are essentially dry. Conversely, sediments are in continuous contact with the overlying water.

Soils and sediments are comprised of organic and inorganic materials whose physical and chemical properties affect sorption and desorption of dissolved constituents. The three major components of soil which have been reported to be of significance to sorption are clay minerals, organic matter, and hydrated metal oxides (Hamaker and Thompson 1972).

In addition, soil texture or particle diameter distribution is of great importance. Soils and sediments are generally described by their sand (2 mm to 50 μm diameter), silt (50 μm to 2 μm), and clay (<2 μm) content. There are 12 named textural classes (Ahlrichs 1972). Texture is important in the evaluation of potential fate of materials because specific surface areas of soils of various textural classes vary markedly. Typical values of specific surface areas for different textural classes have been give by Kohnke (1968). The surface area of coarser materials can be greatly increased as a consequence of a high humus content. However, for sediments, sand or larger size material, surface area is relatively unimportant with respect to sorption of compounds and may be physically excluded from sorption studies. Later, mathematical corrections can be applied to relate the experimental results to those conditions existing in the natural system.

Clay minerals present in soils and sediments may also differ in a number of important properties (Weber 1972). Both clay mineral composition and texture are of importance with regard to hydraulic conductivity though the physical test conditions are of controlling importance.

The organic matter present in soils and sediments may greatly modify the sorption properties of clay minerals. Hamaker and Thompson (1972) cite the results of a number of studies which report increases in the sorption coefficient, K_d (given by equation 2), obtained on the addition of straw, roots, fungal mycelia, live or dead yeast, and flocculent bacteria but changes in sorption properties may not be permanent. The addition of straw to soil initially increased both organic carbon content and K_d for propazine (untreated soil, 0.54 percent carbon, $K_d = 0.78$; freshly prepared soil and straw, 2.08 percent carbon, $K_d = 1.53$; after 81 weeks, 1.20 percent carbon, $K_d = 1.30$). Weber et al. (1979b) have further illustrated the role of the organic layer in sorption of PCB's by sediment materials.

Organic matter has been fractionally removed from soil by Shin et al., (1970) and the residual matter used as a sorbent for DDT. These data, summarized by Hamaker and Thompson (1972), suggest that simple extraction may serve to remove materials whose presence prevents access to sorptive sites, but after H_2O_2 treatment to remove oxidizable carbon the remaining sorptive capacity is only a fraction of that of the initial material.

A large number of studies have been conducted in which the sorption of various compounds has been related to texture, anion and cation exchanger capacity, and organic carbon. Of these, the relationship to organic carbon, over a wide spectrum of soils and compounds, is the most important for synthetic organics and many organometallics. Although there is a reasonable amount of information which indicates the significance of the role of organic carbon content in sorption-desorption reactions on soils and sediments, further research is required to confirm, extend and quantify this relationship. Data currently being compiled by an ASTM Task Group charged with developing a sorption/desorption protocol (Laskowski 1978) indicate that the extent of sorption of the test compound, nitrapyrin, can be closely correlated with the organic carbon content of the test soils.

Studies by Adams and Li (1971) on sixteen Minnesota soils indicated that the variability in lindane adsorption was almost entirely attributable to the organic carbon of the soils. For a series of four lake sediments, organic matter content was found by Lotse et al. (1968) to be more important than clay content in predicting the extent of lindane sorption. However, as by Bailey and White (1964) have indicated, parameters other than organic carbon may, in some circumstances, be of greater significance in controlling sorption. This is particularly true for ionizable compounds such as naptalam (n-1-naphthylphthalamic acid).

No single soil or sediment parameter can account for the observed sorption of various compounds. There appear to have been no systematic sorption studies in which both a range of sediments and soils and of sorbates have been employed. Helling (1971) has reported one related leaching study in which a matrix of 13 pesticides and 14 soils was investigated and multiple regression analysis employed to elucidate the relative importance of selected soil parameters affecting pesticide movement. The results of similar investigations with respect to sorption reactions would be of substantial value in defining the limits of predictability of sorption-desorption phenomena for soils and sediments, as well as in providing information on the sorption behavior of a standard series of compounds.

Such information is necessary to provide a data base with which to compare the results of other studies, including those for screening new materials. This information is of particular importance in the case of sediments for which it may be impossible to provide a "bank" of materials to be used as sorbents. Soils may be air-dried prior to the sieving and homogenization steps necessary for preparation of a characterized materials suitable as a reference sorbent. Conversely, if their significant properties with respect to sorption reactions are to be maintained, sediments cannot be dried. Size separation is achieved by sieving and settling of slurries, and prolonged storage of sediments can result in major alterations as a result of oxygen depletion, biochemical activity and coagulation. It is recommended that the time lapse between sampling and testing be limited, and the conditions of sampling and testing be rigorously controlled. To assure validity of the data, sorption of selected reference compounds of known behavior should be simultaneously measured. Such an approach will likely provide data which could be extrapolated to a wider variety of conditions. It is also recommended that the effects of drying of sediments on the sorption of various classes or organic compounds be established.

3.7 LAND DISPOSAL OF WASTES AND CHEMICALS

Land disposal is not a basic process affecting transport and transformation in the same sense as sorption, diffusion or volatilization, but the land disposal facility is a source of potential movement of materials into soil, air, and water. The physical and chemical characteristics of concentrated wastes disposed directly on land have such a significant effect on the procedures for studying basic processes that land disposal is treated as a separate topic in this section. Additionally, research on site monitoring and site selection (not discussed elsewhere) are needed both to improve disposal practice and to check the effectiveness of new practices.

Land disposal involves a number of practices including landfilling, land cultivation and spreading of microbially degradeable wastes, and overland runoff treatment of dilute wastes. There is a great range in the physical and chemical characteristics of wastes, and in the characteristics of aqueous extracts of wastes and the non-aqueous liquids that drain more or less freely from the waste. Procedures for measuring sorption-desorption properties of substances have been developed for aqueous solutions containing low levels of the materials of interest as well as low levels of other dissolved substances.

The work by Griffin and Shimp (1978) is an example of a sorption study that has been conducted with high levels of other substances in solution. Leachates and other waste liquors are known to have higher levels of dissolved materials (Houle et al. 1978), are more viscous, and may have one or more non-aqueous phases. Measurement of sorption-desorption parameters for single substances from such liquids is expected to require substantial modifications of current procedures. Aeration status in the soil at the disposal facility must be considered, and if wastes will be subject to leaching under anoxic conditions the waste must be similarly leached or extracted. If waste leachates/fluids will pass through anoxic and oxygenic soil, adsorption must be measured under both conditions.

A related problem is development of an appropriate background solution for sorption studies. Background solutions for municipal-waste-landfill-destined substances would be different from those of substances destined for land-spreading or industrial waste landfills. Some work has been done with municipal solid waste landfill simulants (Mitre Corporation 1978), but none for simulating industrial waste landfill leachates which result from the mixing of large numbers of different wastes.

The permeability of undisturbed and compacted soils at disposal facilities is measured using water as the liquid even though such facilities commonly hold mixtures of water and organic liquids. Lee (1978) has shown that mixtures of water and organic solvents flow through clay mineral samples at different rates than does water alone. This effect must be considered when designing landfills and lagoons, and when attempting to predict leaching rates at such facilities.

Another route for loss of materials from disposal facilities is volatilization and vapor phase transport. The amounts and rates of loss by this route are not known; some studies of vapor concentrations have been made (Oberacker 1978; Arozanena 1978) but available information is not sufficient to determine whether amounts lost by this route are substantial enough to warrant concern about specific types of disposal facilities. Farmer et al. (1978) reported a procedure for estimating flux from low-to-moderate vapor pressure, low-solubility organic wastes, using data on soil air-filled pore space and on the vapor pressure of the waste constituents. The procedure has not been tested in the field and it is not known how well the method will predict vapor flux through soil covers over organic wastes with high vapor pressure. Until this tool is further developed and field tested, evaluation of transport from land disposal facilities into the atmosphere will be difficult.

Problems relative to collecting and interpreting data on chemical composition of waters in saturated and unsaturated zones of the soil will limit evaluation of aqueous transport from disposal facilities and collection of information for developing methods for evaluating disposal facilities. Devices for extracting water samples from unsaturated soils have been developed for agricultural use but have not been extensively tested on leachates from disposal facilities under field conditions. Cartwright et al. (1978) have installed pressure/vacuum lysimeters under and around landfills in central Illinois and report success with the technique. A closely related problem is taking a groundwater sample representative of the chemical composition of water at specific points in the formation. Regarding the numbers of well volumes to be removed from a monitoring well before the sample is collected, there are recommendations ranging from 3 to 10 well volumes, or pumping until electrical conductivity is constant. In one instance (Gibb et al. 1978), the concentration of zinc in solution in the eighth well volume pumped was 20 percent of the original value and appeared not to have stabilized. Until this uncertainty is resolved there will be doubt about the accuracy of monitoring well data which will inhibit development and verification of predictive methods for pollutant movement.

Even when accurate groundwater monitoring well data can be collected at land diposal facilities, the problem of predicting concentrations at a point of water withdrawal distant from the facility still remains. Much work related to this topic has been conducted, but the information has not been put into the form of a procedure useful under different hydrologic conditions and different types of disposal facilities.

Finally, tested procedures for predicting the impact of a disposal facility are not available. Although soil is known to have significant capacity for removing constituents from waste leachates, the rates and amounts of removal cannot be quantitatively predicted, nor can the long-term leaching behavior of the waste (the input term) be simulated. The lack of this capability promotes a very conservative approach to design of disposal facilities and makes it impossible to determine the maximum amount of waste loading that may be placed in a facility with a given amount and type of soil between the facility and water bodies that may be impacted. A long time (~10 years) will be required for development of conceptual models for this purpose though empirical procedures can be developed in a shorter time (U. S. Environmental Protection Agency 1978).

3.8 THE USE OF MICROCOSMS IN TRANSPORT AND TRANSFORMATION RESEARCH

Controlled model ecosystems, or microcosms, may have the potential for revealing certain information regarding the transport and fate of chemicals in the environment. The degree or extent to which this information can be extrapolated to the macroenvironment is markedly dependent upon how well the microcosm simulates actual transport and transformation processes operative in natural systems.

It is impossible to incorporate a full range of environmental dynamics in a bench-scale microcosm system. Larger systems which might provide a reasonable simulation of a full range of conditions are necessarily more complex and costly, but promise better reliability with respect to at least qualitative prediction of the fate, transport, and potential impacts of chemicals in the environment. Smaller and less complex microcosms may provide insight into the fate and movement of a compound within one compartment of the environment, e.g., through a particular soil column.

A significant disadvantage of small, single-compartment microcosm systems is the lack of a method for coupling with other environmental compartments even though the dynamics of chemicals in the environment are remarkably influenced by intercomponent phenomena. Examination of only intracomponent factors in simple bench-scale microcosms may lead to conclusions which prove erroneous in natural systems because of intercomponent reactions. The limits of extrapolation from small and simple microcosms must be fully recognized.

Given the previously discussed constraints, appropriate microcosm systems may prove useful as research and screening methods for developing a better understanding of the transport and transformation of chemicals in the environment. If properly designed, such microcosms might:

- Provide preliminary information on anticipated losses via various routes, the rates of those losses, and the ultimate consequences in terms of concentrations in soil, air, water and biota;
- Demonstrate the utility of a given monitoring procedure or instrument in a practical setting;
- Provide opportunity for determining precision of predictions of environmental transport and transformation from elementary laboratory data on physicochemical and biochemical properties;
- Demonstrate the effects of different environmental conditions, altered components, or alternative routes of entry of chemicals into potential target and non-target environments; and
- Provide for testing of interactions between components and processes in a more complex system approaching respresentation of actual environments.

Microcosm systems can avoid the risk of irreversible damage to natural ecosystems or human beings since they are "contained" or "bounded" systems. Structure, composition, operations, and environmental conditions are under the control of the investigator and may be arranged for specific experiments. This control of experimental factors allows attention to be directed to the processes involved in transport and transformation and to the inherent variability derived from natural biologic systems, rather than to uncontrolled environmental forces. Hundreds or even thousands of chemicals might be tested in a microcosm, whereas only dozens of chemicals can be so thoroughly investigated in the field. The results of transport and transformation studies in a rigorously designed and controlled microcosm can be expected to reflect the outcome of the properties of the chemicals and interactive processes involved, particularly when employed in a comparative manner. Systems can be made site-specific (e.g., soil core microcosms) and permit certain biologic effects to be assessed directly with exposure to a chemical (Van Voris et al. 1978). However, microcosms are not self-sustaining, cannot contain all processes represented in the environment, and may not operate validly for long time periods. There are also practical limits to compexity and scale.

To the extent that microcosms validly represent real environments, they can be used to test mathematical models developed from basic properties and potentially reveal discrepancies in the model or disclose unknown processes for transport and transformation. In particular, this approach requires rigorous process and systems analysis thus strengthening comprehension of the general principles involved in transport and transformation.

Caution should be exercised because "verification" of mathematical models in microcosms does not ensure their validity for predicting conditions in the real environment; they must be modified and specifically tailored to account for differences between the micro and macro systems. This is particularly true if such models are both calibrated and verified with microcosm data. There is a definite need for research on the extrapolation from small microcosms to more complex microcosms and to actual environmental systems.

Preliminary studies reviewed in Gillett and Witt (1979), and evaluated by a peer panel in great detail, have demonstrated that there are several terrestrial microcosm systems capable of being employed for testing environmental movement of chemicals (leaching or soil percolation, volatilization) and transformation (loss of parent material, appearance of metabolites and "bound residues"), including bioaccumulation. The soil core microcosm (Draggan 1976; Ausumus et al. 1979) is the simplest of these systems and shows the greatest promise for use in screening for transformation and soil movement. It is in the stage of interlaboratory testing for both fate and effects assays of pesticides, toxic substances, and industrial effluents.

The Cole/Metcalf systems (Cole et al. 1976; Cole and Metcalf 1979) have been tested with about 20 chemicals, the CERL Terrestrial Microcosm Chamber (Gile and Gillett 1979) with about a dozen, and the microagroecosystem (Nash and Beall 1979) with about ten. These are much larger and more expensive systems and include more extensive sets of tests. These systems currently lack adequate research bases for immediate application to screening systems. The degree of representation of transport processes (scaling, boundary conditions) has not been thoroughly investigated. Transformation processes have been thoroughly studied in the large microcosms and only preliminarily in soil core microcosms. Multi-organism and multi-media tests were judged more representative of actual environmental disposition. Achievement of environmental conditions (media flux, stochastic dispersion of energy and media flux) approximating reality has not been systematically sought, although some experimentation is in progress. Thus far, the systems lack demonstrable photochemical processes. The problems due to added "large" animals (and their attendant effects on structure and abiotic processes) have not been investigated.

Many of these difficulties can be studied and possibly overcome; alterations have already been made in some systems as a result of this review. Full endorsement of terrestrial microcosms cannot be given without further improvement of the present state-of-the-art though many observers believe that adequate laboratory systems can be achieved.

The Gillett and Witt (1979) state-of-the-art review revealed specific areas where information is needed. Continued development is required to assess the degree of environmental control necessary to achieve outcomes of transport and transformation representative of field results. Criteria for operation need to be obtained that will permit evaluation of microcosms of different structure, composition, or operational variables on a commensurate basis. The precision in any given microcosm system needs to be validated by interlaboratory testing and compared against field studies specifically designed for that purpose. Current verification is achieved by comparison to results of monitoring or fate studies under broadly differing circumstances than the microcosm test. Precision and accuracy in microcosm studies need only be similar to field results; because of expectations of greater accuracy, microcosms have often been viewed as unsuccessful.

Mathematical models should be constructed that would predict the outcome of transport and transformation studies from simple laboratory measurements of basic properties of the chemical and microcosm studies compared to the model. Innovative means of data reduction need to be introduced to handle the relative richness of microcosm outputs. Cost-effectiveness studies of microcosms should be conducted to determine if various sets of tests can be replaced with the simple soil core microcosm.

The foregoing discussion indicates several thrusts of terrestrial microcosm research. The most appropriate screening systems need to be validated by interlaboratory testing on the same chemicals from broadly differing classes. Subsequently, validated microcosm systems need to be verified in specifically designed field studies. The variation between laboratory and field systems needs to be carefully determined, particularly with respect to the impact of variables such as temperature, wind and water flux, soil type, and mode of application of the chemical. The range of results for transport and transformation need to be more thoroughly explored within specific classes of chemicals (e.g., an extensive homologous series) and between widely differing chemical classes for which some environmental data in the field are available. Data management models and mathematical models of transport and transformation need to be set forth. Operational simplification should be investigated, particularly aimed toward developing the necessary and sufficient information to predict likely environmental fates.

One of the chief objectives of microcosm technology is the development of systems which can be used to carry out research on interactive processes and thereby predict the results of competing properties expressed as elementary characteristics of a chemical (e.g., sorption, solubility, volatility, sites of chemical transformation). Of primary concern is whether or not realistic air and water flows could be achieved such that transport processes would be adequately simulated in the laboratory. Moreover, the lack of modeling is a major concern.

Clearly, the more complicated systems appear to have greater utility in this phase of microcosm application, since temporal and spatial studies could be performed. Hence, one might divide terresterial microcosms according to whether they would be applied to screening (highly standardized, limited focus) or to research on processes such as vapor loss, leaching, bioaccumulation, and biotransformation (more complete as to processes and levels of complexity included, broadly focused). The former might be tested against many chemicals and involve variable substrates and environmental conditions. The latter would be employed with only a few chemicals and carefully constructed and operated for comparison to a specific field situation. It is through this latter approach that Gillett and Witt (1979) believed that mathematical models might be extended to the field via microcosm studies and complete the predictive sequence from basic laboratory bench data on physical and chemical characteristics. In this iterative process, the reviewers felt that the microcosm would thereby be an intermediate technology permitting extension ultimately from the basic data with relatively few confirmatory tests in the microcosm or field. Such a predictive capability would greatly reduce the cost of testing for screening purposes, provide better understanding of the complexity of the interacting environmental processes, and permit attention to be directed at application of mathematical and laboratory model systems to other aspects of chemical control.

Terrestrial microcosms for predictive techniques suffer the same problems in terms of data deficiencies as for screening and testing techniques. Due to the predictive focus of this report, the absence of adequate modeling efforts is particularly acute. Moreover, the validation and verification efforts would necessarily be more extensive, and more expensive, for this class of investigation. The problems of necessary and sufficient studies of scale (size), scope (relative complexity), and data "richness" are amplified in larger and more complete systems. Criteria need to be established for determining just how accurately a microcosm must represent field experience given the problems of spatial and temporal heterogeneity and instability of environmental variables in the field. These criteria must then be applied to determine the need for accuracy of environmental controls in microcosm operations, the detail of chemical tests to be applied, and the extent of data resolution. It would not be cost effective to demand of microcosm systems a degree of accuracy unachievable in natural systems.

3.9 SUMMARY OF RESEARCH NEEDS

The soil and sediment group did not prioritize their research needs because it was felt priorities would be impossible without some type of budget framework. As a result, the following recommendations are listed in the order in which they appeared in Section 3.

1. Relate the structure of chemicals to sorption over a wide range of soils and sediments, and the effects of soil/sediment surface and structural properties to sorption/desorption reactions. Study the prediction and measurement of linear free energy relationships between chemicals and soil/sediment surfaces. These studies should include evaluation of other particulate solids - such as fly ash, plant residues, street dirt, etc., - which function as sorbents and transport media for toxic chemicals in the environment.

2. Develop an extensive reference library of sorption/desorption data on different chemicals and soil/sediment systems. This should include reference soils and sediments and reference classes of chemicals.

3. Quantify and evaluate the significance of long-term sorption and desorption kinetics. These studies should include characterization of the chemical state of the sorbed species to provide a better basis for predicting and understanding sorption and transformation reactions in the environment.

4. Determine the effects of various types of soil/sediment preparation, sterilization, and storage techniques on the sorption/desorption, organic, and biochemical character of these sorbents.

5. Determine the effects of cyclical variations in soil temperature and moisture content.

6. Verify the applicability of normalizing sorption on sediments and soils to carbon content, K_{oc}, and/or octanol/water partition coefficient. Determine with which types of chemicals and/or soils these predictive methods are inappropriate.

7. Determine and quantify the importance of mixing processes between sediments and overlying water, and between soils and overlying air, as they affect uptake and release of contaminants. These processes include hydro-dynamic dispersion, physicochemical disruption, and bioturbation.

8. Develop mathematical models for predicting transport of soil and sediment materials - and associated chemicals - through the atmosphere and water column, and the possible differential accumulation of these materials in various compartments of the environment.

9. Study and establish methodologies for measuring chemical sorption by ferric oxides in sediments, as affected by redox potential changes. Study how widespread the occurrence of sorption onto ferric oxides is in nonsediment environments, such as soils and drainage systems.

10. Improve reliabilty and availability of vapor pressure data on specific chemicals to allow assessment of volatilization losses from soil, water, and plant surfaces.

11. Improve data collection and uniformity of laboratory and field leaching simulations. To predict leaching in landfills determine how sorption reactions in soils are influenced in the presence of the leachate. Improve capability for predicting leaching in the natural environment by accounting for spatial variability.

12. Develop thorough knowledge of the chemistry of metals in soils and sediments to enable long term predictions of the transport of heavy metals, including the effects of added complexing agents in regard to release of metals from amended and unamended soils and sediments.

13. Develop predictive models for leaching and diffusion which include appropriate degradation terms.

14. Develop, refine, field test, and validate models for prediction of transport of chemicals by run-off from non-point sources.

15. Determine the particular circumstances under which photodegradation on soils and sediments is important, and the physicochemical properties and/ or structure-activity relationships that are needed to predict photochemical transformations.

16. Determine conditions that are appropriate to simulated laboratory tests, and which must be measured in field experiments, in order to generate photodegradation processes of environmental significance and identify their pathways and products.

17. Characterize the photodegradation of chemicals on airborne particulaltes or in the vapor phase following volatilization from soils and/or sediments.

18. Develop and test models for predicting vapor loss of various organic chemicals from soils. These models include simultaneous movement of the chemical toward the surface by diffusion and mass flow in evaporating water, while at the same time considering changes in concentration from degradation of the chemical in the soil.

19. Determine an approprite set of reference or benchmark compounds that can be exhaustively tested in field studies and model ecosystems to permit testing, calibration, and verification of predictive mathematical models.

20. It is important to determine the relative degree to which particular synthetic organic compounds are acted upon by biotic or abiotic mechanisms, what structural characteristics are correlated with or account for resistance to abiotic transformations and to microbial mineralization or co-metabolism, and how mineralization and/or co-metabolism reactions can be enhanced.

21. There is a need to determine the role of invertebrates in transforming synthetic chemicals, either directly or indirectly. Research is also needed on how plants in soils, and macrophytes in waters, transport and transform synthetic chemicals. Uptake of toxic chemicals by plants, and thereby the significance of soils as a reservoir or source of chemicals to animals, should be established.

22. The types of kinetics and kinetic expressions appropriate to biotic and abiotic transformations must be determined to allow for meaningful predictions of environmental behavior of chemicals.

23. The effects of environmental factors on biological and abiotic transformations in natural environments should be explored. The sorption of synthetic chemicals to colloids in soils and sediments as protection against biodegradation requires attention, and the role of oxygen and anaerobiosis in

biodegradation must be clarified. The role of one chemical or a mixture of chemicals in affecting the transformations of specific compounds of interest requires definition, and the influence of concentration on the rate of abiotic and biological transformation of a chemical in natural environments needs to be determined.

24. Test the suitability of existing sorption/desorption procedures for land disposal of concentrated chemicals using liquid wastes and leachates/extracts of wastes to identify problems due to the unique physical/chemical nature of the wastes and to identify needs for changes in the procedures. Develop a simulant for municipal landfill leachate so the sorption/desorption characteristics may be predicted for single components that may go to landfill.

25. Develop information or test procedures for predicting changes in conductivity of landfill soils/clay liners due to organic and inorganic constituents of concentrated wastes. Evaluate reactions and transport of non-aqueous liquids in soils. Develop methods for predicting the rates of movement through soil of constituents of wastes and combinations of wastes placed in specific disposal facilities.

26. Monitor the air around land disposal facilities to determine whether volatilization is producing appreciable air pollution. Develop methods for predicting rates and amounts of release of vapors from disposal facilities.

27. Evaluate devices for taking liquid samples in unsaturated soils at disposal facilities. Develop methods for taking groundwater samples that are representative of the chemical composition of water at a specific location in the water-bearing formation. Using chemical composition of groundwater at specific locations around the disposal facility as inputs, develop methods for predicting the composition of waters at locations distant from the disposal facility and the composition of waters withdrawn from wells (of various design and yield) at such locations.

28. Through interlaboratory testing, determine the precision with which microcosm experiments can be replicated.

29. Determine the accuracy with which microcosms can be used to predict transport and fate of chemicals in field situations, taking into account the variability of replicated field tests. These data are required to evaluate the ultimate utility of microcosms. Determine the applicability of microcosm systems for predicting the transport and fate of several chemicals within each of a wide variety of chemical classes. Ranges of results both within chemical classes and between classes need to be determined.

30. Ultimately develop a mathematical model which is capable of reliable prediction of the transport and fate of a chemical in the environment based upon measurable properties of the chemical and of the major components of the environment, and a reasonable knowledge of the dynamics and interactions of transport and transformation reactions.

The Soils and Sediments Group participants are listed in Table 3-1.

TABLE 3-1. SOIL AND SEDIMENT GROUP PARTICIPANTS

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4.0 EFFECTS OF BIOTA ON TOXIC SUBSTANCES

4.1 INTRODUCTION

This section elucidates the state-of-the-science and research priorities necessary to allow risk assessments of toxic substances through biological components of ecosystems, and focuses on the biological aspects of transport, transformation and storage of toxic substances. The research priorities are oriented towards and constrained by the need to obtain anticipatory assessments based upon generic properties of new substances.

In general, predictive techniques should be based upon mechanistic processes. Many of these processes have been discovered and analyzed in simplified, laboratory conditions. It is essential to evaluate the utility and limitations of incorporating laboratory studies into ecosystem models. Many of the recommendations involve efforts to identify and quantify factors of complexity and scale as one goes from prototype to full scale systems.

Further information is needed on the biotransformation of substances in particular environments. Microbial activity, particularly in anaerobic environments, needs considerable articulation. The role of higher organisms is unclear and this issue should be resolved at an early date.

The transport of toxic substances by organisms has seldom been quantitatively analyzed. A few classic case studies exist which are natural opportunities for analysis of regional transport. The kepone episode in the Chesapeake Bay is probably the best example since the input took place at a single point in space and time.

This chapter is the consideration of opinions of some sixteen individuals (Table 4-1) who are currently involved with research and regulatory activities associated with toxic substances in the environment. Their discussions focused on the biological data required to formulate and initiate predictive models dealing with biotransformation and biotransport. Furthermore, they concentrated on specific research recommendations that could be realistically initiated and completed. The recommendations reflect the collective concerns at the time of the conference (December, 1978). The issues are arranged into seven sections each accompanied by a short explanatory statement. The recommendations are incorporated into the appropriate text.

4.2 BIOTRANSFORMATION

A vast amount of literature exists on the biochemical pathways through which various toxic substances might pass but the primary areas of interest are microbes, higher plants, and higher animals. Ecological analyses have repeatedly demonstrated the critical role of microbes in energy flow and biotransformations of materials. Very few data exist on rate functions determined under field conditions. The interest in higher plants resulted from the increasing use of terrestrial ecosystems for the recycling of municipal and industrial waste waters and sludges while the emphasis on higher animals resulted from questions as to whether or not these organisms have any major direct influence on biotransformation.

Predictive models must be based upon mathematical representations of functional mechanisms if one wishes to characterize unobserved events. Knowledge of the mechanisms of biotransformation at the biochemical level will be needed for certain types of processes. The emphasis on standardized in vitro analogs for activation and detoxification processes is motivated by the need to express causal mechanisms in the desired models.

4.2.1 Microbial Transformations

Microbial degradation is important to the fate and transport of a chemical in the environment. Little is known concerning biodegradation in nature and most of our current information on biodegradation results from laboratory studies in which selected pure or mixed microbial cultures were used. A major question remains concerning the validity of extrapolating these laboratory results to the natural environment. Microbial degradation, persistence, and environmental effects on microbial transformations have been discussed previously (see Microbial Degradation of Pollutants in Marine Environments: Consensus to Methodology, Interpretation, and Future Research, 10-14 April 1978, Pensacola Beach, Florida).

Currently, rate constants for microbial degradation or transformation are obtained in the laboratory from pure cultures utilizing a given chemical as a sole carbon source. These methods may generate environmentally unrealistic information because co-metabolic phenomena could have a significant effect on degradation yet involve minimal changes in microbial biomass or physiological activities. Verification of in situ rate constants should be undertaken and the influences of environmental parameters on rate constants should be defined. It remains to be determined whether a measurement of the physiological activity of microorganisms (ATP, lipids, heterotrophic uptake) may provide a useful basis for comparison between laboratory and environmental systems.

Much of the natural environment is anaerobic. Unfortunately, little is known about the microbial degradation processes and the transformation products of chemicals under in situ anaerobic conditions. Such information on the anaerobic microbial process is crucial for predicting the fate of chemicals in the environment.

In addition, anaerobic microbial degradation should be investigated to determine the effects of anaerobic treatment plant effluents, anaerobic microflora of the human and animal gut, and the microbial reactions that occur in sediments. More suitable methodologies are needed for easily studying the anaerobic process in the laboratory.

Natural and synthetic organic nutrients often occur in very low concentrations and bacterial populations in aquatic environments are specifically adapted to growth at these low nutrient levels. Thus, common naturally occurring organics such as urea, glycollic acid, and amino acids may be biodegraded in preference to synthetic organic pollutants. Consequently, threshold concentrations of pollutants may exist in nature below which degradation will not occur. Similarly, due to concentration effects and preferences for naturally occurring organic nutrients, microbial populations in natural environments may never become adapted for specific degradative capacities. The effect of concentration must be experimentally verified using laboratory and field degradation studies which specifically maintain low pollutant concentrations.

Most available information concerns microbial biodegradation and little is known concerning biodegradation by fungi, algae, and protozoa. Efforts should be undertaken to define the mechanisms and pathways of biodegradation for these other organisms.

4.2.2 The Fate of Toxic Materials in Higher Organisms

4.2.2.1 Plants

Although the chemical and physical properties of toxic substances determine their transport and fate, at present neither the action of new chemicals in plants nor the effects of vegetation on the fate of these substances can be predicted. A great deal is known about the fate of toxicants in or on plants (U. S. Environmental Protection Agency 1975).

Plants can translocate substances downward from leaves to roots and other organs or in the reverse direction depending on the point of entry, the physical state, and chemical properties of the materials. Substances can preferentially accumulate and be stored in certain organs in their original form. They can add to and be indistinguishable from existing amounts of these same substances accumulated from natural sources. They may undergo transformation resulting in storage of degradation or reaction products which can be more or less toxic than the original substances. Materials can move from the interior of plants by exudation to leaf or root surfaces where they can be lost by the action of rain or dew (leaching), wind, abscission, or as a result of consumption by herbivores or omnivores. Loss of organs to soil can lead to further conversion or degradation by microorganisms, storage in soil, or transfer to water supplies. Some substances can be volatilized from plants directly to the atmosphere.

As a consequence of these manifold and complex processes taking place in vegetation, research is needed to derive both general principles and quantitative descriptions for the construction of predictive models. The question is, which processes deserve highest priority?

The most important factors concerning the transport and fate of toxic substances in plants are degradation and conversion of toxic substances to more or less active forms (metabolism), the extent to which plants transfer substances to other media (soil, water or air), or to other organisms, and the degree of accumulation of toxic substances in plants and the conditions under which this accumulation is fostered or inhibited.

4.2.2.2 Animals

Animals affect the fate of exogenous chemicals either directly through assimilation and metabolic transformation, or indirectly through their control in the structure and microbial activity of ecosystems.

Direct uptake by feeding assimilation and metabolic transformation of chemicals by individual animals can be studied in the laboratory (greenhouse and metabolic cage studies). It is not apparent that this work has been systematically used to estimate the magnitude of importance of these biotransformations on the environmental fate of chemical pollutants. For example, benthic aquatic insects and terrestrial invertebrates consume and process great quantities of detritus and soil but there is little knowledge of the importance of these groups in directly biotransforming chemicals in relation to the microbial populations present. Fish, aquatic and terrestrial crustaceans, and bivalves should be similarly examined.

Animals are important in influencing the active microbial biomass present in aquatic and terrestrial systems. They would, therefore, be important factors in indirectly determining the capacity of a system to biotransform chemicals microbially. The microbial stimulation from the bioturbation and detritus-processing activities of invertebrates in sediment and soils provides examples of the influence that animals have on microbial activities. The alteration of microbial biotransformation rates occurs as a result of organisms incorporating chemicals into microbially available forms (zooplankton, fecal pellets, animal tissue).

Higher animals may also indirectly affect microbial biotransformation of chemicals by controlling the movement and concentration of these materials in systems. Uptake and excretion of a chemical in a more concentrated waste product may affect biotransformation rates in microbial populations utilizing those wastes as substrates. Nesting, food storage, and waste disposal activities may also affect local concentrations of chemicals.

Experimental manipulations of animal species have been shown to have significant impacts on the structure and function of ecological communities (Paine 1966; Hall et al. 1970; Neill 1975; Dayton 1971). Changes in foraging patterns, prey selectivity, competitive interactions, and habitat modifications associated with alterations in species arrays will affect the composition and abundance of the microbial fauna and flora. This feedback of effects will directly influence the biotransformation capability of a given ecological community. The primary role of higher organisms might not be apparent from studies oriented solely towards activation and deactivation potentialities.

Work with artificial outdoor streams has shown that removal of crayfish from these systems resulted in notable changes in the stream species composition. Mechanical exclusion of crayfish, aquatic insects, or other important detritus-processing groups from similar streams could demonstrate the effects such exclusions have on microbial activity and biotransformation of chemical contaminants.

4.2.3 In Vitro Activation/Detoxification Models for Whole Animal Biotransformations

4.2.3.1 Biochemical Investigations

Standard methods to use microsomal mixed-function oxidases should be developed and utilized. Representatives of various animal groups, including those which are commonly used in laboratory studies (rat, mouse, chicken, bluegill or other fish, insect, etc.), or those which are important in regard to transport and fate of toxic chemicals, should be utilized. The investigator studying the metabolism of the toxic chemical and the mixed-function oxidase should provide information about the activity of the enzyme system towards some standard assays such as aldrin epoxidation (Stanton and Khan 1975), aniline or benzopyrene hyroxylation, and O- and N-demethylations of, respectively, para-nitroanisole and d-benzphetamine, and cytochrome P-450 contents (Omura and Sato 1964; Mazel 1972; Burke and Meyer 1975). Microsomal oxidases are an important detoxification system and perform aliphatic and aromatic hydroxylations, O- and N-dealkylations, desulfurations, and hydrolysis. The levels of activity of this system in various animals should be known and included in the ecological models.

4.2.3.2 Other Detoxification Systems

Microsomal enzyme systems such as epoxide hydratase attack epoxides, many of which are known carcinogens. The effects of these enzymes on epoxide or oxides of toxic chemicals should be investigated to understand whether the epoxide intermediates produced in animals in the ecosystem will accumulate or be further metabolized (Oesh et al. 1971; Bentley et al. 1978). Other microsomal enzyme systems such as glucuronyl-transferases and esterases should be investigated as their activity will indicate whether certain ester type toxic chemicals can be hydrolysed. The investigation should also show whether the animal is able to further handle, by conjugation, the metabolites of the toxic chemical (Doroug 1979; Yang 1976).

Cytosolic detoxification systems include esterases, conjugases of various kinds, glutathione-dependent transferases, and dechlorinases (Yang 1976; Doroug 1979; Dauterman 1976; Hollingworth 1976). These enzymes should be used as models to understand the ability of the test animal(s) to metabolize toxic chemicals. These detoxification systems are standardized in certain laboratory-reared mammals, fish, and birds and it will be easy to use them as models for the study of the fate of the toxic chemical in vitro.

The selection of test animals should include animals that are most commonly used in the laboratory, easily raised in the laboratory, easily obtained from the field, and play an important role as target or non-target organisms in the ecosystem regarding the fate and transport of the toxic chemical. It is also recommended that radioactive tracers should be used and sufficient analyses be carried out to chemically characterize the nature of these biotransformations.

4.2.3.3 The Use of Laboratory Obtained Parameters in Estimating the Distribution of Organic Compounds in Environmental Compartments

It has been shown in hundreds of examples that log P(P = octanol/water partition coefficient) can be used to correlate the binding of organic compounds to proteins, fat phases, tissue, soils, and fabrics as well as the movement of organic compounds through various membranes (natural or synthetic). Equations of the following type are found to hold:

$$\log k = a \log P + c \qquad (1)$$

$$\log k = a \log P + b (\log P)^2 + c \qquad (2)$$

k may be a rate or equilibrium constant. Neely and co-workers at Dow have shown that for a very small stable set of pesticides equation (1) held for the uptake by trout. However, this study plus some work by Metcalf's group is so limited that one can be quite sure it will not hold for a large set of organic compounds in a real ecosystem. Such a large set of compounds would have varying degrees of chemical and biochemical reactivity through which they would be modified and hence their distribution affected. One might expect the following general equation to hold:

$$\text{Conc. biophase}_i = f\ (\log p, \text{ Special Reactivities}_i) \qquad (3)$$

There are a large number of special reactivities and it appears that microsomal and photochemical processes are two of the most important. In addition, hydrolysis is important but might be lumped in with photchemical in a single parameter. With these parameters:

VP = Vapor pressure

MO = Microsomal oxidation

PC = Photochemical Change

Hyd = Hydrolysis

which would be relatively easily determined under a set of standard laboratory conditions, a correlation equation could be formulated:

$$\log \text{Conc. Biophase}_i = a \log P + b (\log P)^2 + d\ VP + e\ MO + f\ PC + g\ Hyd + c \qquad (4)$$

Once a-f are established for a representative set of chemicals found in the various phases of a microecosystem, the fate of new chemicals could be estimated.

This stochastic model assumes that octanol/water partition coefficients will be a good approximate measure of the thousands of lipophilic/aqueous partitioning ratios organic compounds will experience from source to sink. This has been established to be true for a drug passing through animals where partitioning is occurring with thousands of different macromolecules, fat depots, and membranes.

In an ecosystem there are thousands of biochemical degradation systems. The rat-liver microsomes $^{(S-9)}$ could represent a prototype in the same way octanol/water partitioning approximates movement through thousands of different lipophilic phases in an animal. One cannot consider all possible routes of biodegradation. Hence, the stochastic approach appears better than a deterministic model.

4.2.3.4 The Utility of Biochemical Processes in the Macroscopic Models

Incorporation of biochemical processes into macroscopic population models requires several levels of system integration. This activity is extremely complex and requires considerable scientific documentation. Prototype systems should be selected for which population, community, and ecosystem data currently exist.

The following series of analyses should then be initiated:

1. Organisms from various phyla important in the ecological concentration of the toxic chemical or those that can be raised in the laboratory should be used, e.g., Daphnia, mussel, lobster, fish (bluegill, carp, goldfish), bird (chicken, duck), mammals (rat, rabbit).

2. The physiological state of the organisms should then be described. This includes age, size, sex, nutritional status, season of the year and previous exposure of the animal to other xenobiotics.

3. The routes of exposure of the test organisms should be determined. For example, absorption of the chemical can occur from the aquatic environment, ingestion of suspended particles in water, or consumption of detritus, animal or plant tissues.

4. Standard methods used by other federal agencies (FDA, NIH, USDA and USEPA) should be reviewed to determine the protocol for such studies.

5. Bioaccumulation studies of chemicals should use standard procedures for such assays. Existing procedures should be further improved to make them adaptable for these studies. Most bioaccumulation values are derived from the concentration of the toxic chemical in the whole animal. It is recommended that, in addition to the concentration within the animal, the concentration of the chemical in certain specific tissues (such as muscle, liver, kidney, brain, gonads, fat) should also be described. This may eventually lead to physiological models of the toxico-dynamics of the chemical in organisms. This is a necessary step in the integration process.

6. The half-life of the chemical in the whole organism as well as in various organs of the animal should be determined. Standard methods to study this should be outlined to be used by investigators to provide data for the regulatory procedures.

The previous information on bioaccumulation, storage, metabolism, and elimination by various animals in the laboratory should be integrated with knowledge of the population dynamics of these species or similar species in prototype ecosystems to determine the magnitude of importance of biochemical transformations by higher organisms.

4.2.4 Biotransformation Recommendations

Rate constants for biodegradation of toxic organics regulated by EPA should be defined. The influences of environmental parameters, nutrient concentration, chemical concentration and microbial populations on biodegradation rates should be tested in laboratory and field systems. A determination of the feasibility of using various physiological parameters to relate the result of laboratory and natural biodegradation processes should be included.

Methodologies should be developed for easily studying and screening anaerobic microbial transformation processes in the laboratory. Much more information is needed concerning the magnitude of anaerobic microbial transformation of toxic organics in prototype environments (marine sediments, flood plains, saturated soils).

The role that other microbial forms (fungi, algae, and protozoa and their communities) play in degradation or transformation should be determined. Pathways for degradation or transformation by these other microbial forms should be studied for prototype ecosystems of particular concern.

Prototype plant species should be selected based upon their use in human food chains or their dominant role in critical ecosystems. The role of higher plants in biotransformation and microdistribution should be systematically investigated utilizing organic and organo-metallic complexes as test chemicals. Emphasis should be given to those residuals commonly found in municipal sludges.

Field plots should be examined for the effects of various populations of higher plants (monoculture and mixed communities) on the rate of microbial biotransformation of chemical contaminants.

Utilizing a well studied, experimental ecosystem, the relative magnitude of direct and indirect effects of higher animals on biotransformation of chemicals in the environment should be more systematically assessed and compared with microbial transformation rates in similar systems.

The environmental importance of direct biotransformations described in metabolism cage studies with individual organisms must be evaluated and the factors affecting the initial uptake and assimilation of environmental chemicals by populations of higher organisms must be determined. A knowledge of community-level interactions (predation, competition) will be important in making the extrapolation from single organism metabolism studies to environmental biotransformations by populations.

A few key ecosystems frequently exposed to exogenous chemicals should be examined in the above manner to determine the indirect effects of higher animals on microbial biotransformation.

A program for development of a series of in vitro systems utilizing microsomal and specific enzyme activation and detoxification processes should be initiated. Prototypes should be selected that are feasible and available to general laboratory operations. Furthermore, the prototypes should reflect critical ecological components influencing the transport and fate of toxic substances. Utilization of these physical prototypes should be a standard aspect of the assessment protocol.

A reasonable start for the stochastic approach might be to analyze five sets of twelve congeners each. Families such as chlorinated hydrocarbons, phenols, aromatic amines and phosphate esters with good variation in physicochemical properties in each should be carefully selected. Important industrial chemicals must be included with other molecules. Crucial to the project is a reasonably good microecosystem on which to validate parameters. Such a project would best be done as a cooperative effort by several laboratories with expertise in each area including a photochemist to get photochemical constants, a laboratory experienced in working with microsomal oxidation, and an environmental lab with experience with microecosystems.

Prototype ecosystems should be selected and utilized to document the procedures of integration across levels of structure in the ecological hierarchy of complexity. This integration includes the mechanisms of transformations and the magnitudes of the activity given population and community characteristics.

4.3 BIOLOGIC TRANSPORT

4.3.1 Existing Case Study

Since many species of animals and plants move from one location to another due to migration or translocation by air or water currents, the biological mode of toxicant transport should be incorporated into mathematical models. The particular life cycle or feeding characteristics of an animal may influence the distribution of a substance in the system. Therefore, the biological segment of the ecosystem should be recognized not only from a toxicological or biotransformation standpoint but also as an active transport mechanism.

Many harmful substances, such as PCB's and pesticides, have entered the ecosystem from varied sources which confuses the interpretation of field data relative to biological transport. An exception is Kepone which has contaminated the estaurine portion of the James River. This compound has been transported from the Chesapeake Bay to New England waters by bluefish and striped bass which were resident in the Bay before migrating north (Huggett et al. 1979). Blue crabs in North and South Carolina have been shown to contain Kepone, presumably due to consumption of contaminated fish migrating south from the Chesapeake (Huggett et al. 1979). Even though the amounts transported by these fish are but fractions of a percent of the total amount present in the James River, it is sufficient to contaminate ecosystems far removed from the "polluted source."

Microdistribution can be determined by biotic activity that mixes substances and sediments and concentrates by filter feeding. Kepone penetrates the sediments of the James River far in excess of expected diffusion or sedimentation rates due to the fact that burrowing organisms are constantly mixing the sediments (Huggett et al. 1979). Other examples of the biota influencing the distribution of toxicants exist. The biotic component of transport must be integrated into models designed to predict the transport of toxicants in the environment.

At the present time there are few mathematical models capable of modeling bioaccumulation of toxic substances in complex ecosystems. Currently, none of these are being used to predict biological transport from one part of the ecosystem to another, with the exception of the obvious water column, suspended-sediment coupling. Furthermore, most of the models are based on simplyfying assumptions that are incompatible with the detail required for modeling biotic migration.

An example of a model that can be used to represent this type of transport is PEST (Park et al. 1977; Leung 1978), which considers twenty carrier compartments including four age classes in two groups of fish. With such detail toxic substance loads and migratory patterns can be distinguished for each age class. These can be verified in the field where migratory populations are periodically exposed to point-sources of toxicants. A good example is anadromous fish that come into contact with Kepone as they migrate into the James River and leave with a relatively high Kepone load.

4.3.2 Information System

There is a vast amount of literature on transfer rates between organisms and their environments. Consumption rates, defecation rates, migration patterns, sorption and desorption coefficients, and mortality rates are just a few of the measurements obtained from ecological studies.

Predictions of chemical transfers within ecosystems for regulatory decisions should be based upon measured environmental transfer rates whenever possible. To aid in these predictions, the information concerning chemical transfer coefficients among ecosystem components which currently exists should be abstracted, indexed, and placed on a computer retrieval system. The index system should employ a large array of prioritized key words which will provide maximized cross-referencing.

The abstracts should be worded in a manner which is understandable, pertinent to the hazard evaluator, and readily usable in current hazard evaluation calculations. Tranfer rate data for higher trophic levels should receive priority attention as hazards to macroorganisms are most likely to influence regulatory decisions.

4.3.3 Anthropogenic Influences

The PBB episode in Michigan provides a classic example of the potential for a toxic material to be rapidly transported throughout a region. The dominant process of transport involved the spatially oriented activity of the agrobusiness industry. The accidental addition of the toxicant into an animal feed component of the dairy industry took place at a single location. The materials were then distributed, remixed, redistributed, and eventually sold to production units broadly distributed throughout the midwest.

Attempts to reconstruct the patterns and processes of distribution demonstrated a serious lack of data on the intra- and inter-state transport mechanisms within this industry. A majority of transactions involved independent truckers and farm businesses for which there is no monitoring or reporting system available. In fact, the existing reporting system indicated that the toxic substance failed to cross the political boundary of Michigan.

Similar issues are now surfacing with the residual management of hazardous substances. One should develop the predictive ability to simulate probability isopleths of distributions of a toxic material given a point-source origin, a time period from the initial event, and a pattern of commercial transport. This capability will be of particular importance in the allocation of human and monetary resources to post-episode monitoring.

4.3.4 Transport Recommendations

A model such as that developed by Park et al. (1977) and Leung (1978) should be modified to be applicable to the Kepone incident in the James River. Taking advantage of the existing monitoring program (Huggett et al. 1979), the model should be utilized to predict the distributional pattern of Kepone throughout the Chesapeake Bay and associated waters resulting from the new exposure of migratory fish in the spring. This appears to be a unique opportunity to explore and validate a regional transport model.

An information retrieval system should be developed that would allow those involved in environmental assessment to have rapid access to the diffuse literature involving measurements of transport and transfer rates among ecosystem components. The emphasis should be on coefficients, thus complementing the Toxline system.

Utilizing a specific case study like the PBB in dairy products or the mercury in tunafish, EPA should develop a case history analysis that characterizes the anthropogenic distribution of a toxicant. The analysis should include the man-made transport, storage, utilization, and residual management components. From case history analyses, a determination should be made as to whether or not it is feasible to develop a generic system that predicts distributional characteristics for any given environmental episode.

4.4 MODELS: MATHEMATICAL AND PHYSICAL ANALOGS

4.4.1 Further Studies in Model Development

Most existing biological fate models are point models that ignore the spatial heterogeneity that is so important in a natural system. Such models are adequate for evaluative purposes but are inadequate for assessing impacts at particular sites.

Only a few horizontal and vertical segments are required for many site-specific applications. The connectivity of these segments can be specified by the user on an ad hoc basis. Depending on the model, this may require significant reprogramming. However, at some sites the spatial resolution will be critical and a fine grid encompassing many segments should be employed. Capability for representing this resolution is not present in existing bioaccumulation models. Furthermore, specification of the biologic and physical connectivity of the segments is a monumental task if left to the individual user. Comparable problems have been encountered in modeling thermal plumes in a variety of aquatic systems and algorithms have been developed that can be adapted to bioaccumulation models.

The concept of mass balance is sufficiently accepted as an attribute of systems dynamics so as to need little further elaboration here. Instead, a detailed consideration of where and why the measurement of mass balance has been impractical and/or incomplete should prove valuable. In particular, such a review should examine the way in which mass balance studies are linked to the problems of transport and fate of environmental pollutants. Elemental mass balance measurements are usually the easiest and cheapest but may have little use when toxic compounds and daughter products are the substance of concern. There are exceptions to the ease and cost of mass balance. For example, the measurement of N_2 released from soil and sediments as a result of denitrification is a difficult measurement without the use of isotopes.

Clearly the establishment of a mass balance table in any ecosystem requires clear and unambiguous definition of the boundaries defining the system of interest, knowledge of the transport pathways and rates of movement into and out of the system, the capability of analyzing for the compound(s) of interest, and knowledge of the important physical sinks and sites of bioaccumulation within the system so that an adequate sampling program can be designed. Thus, a mass balance study is directly related to the details of transport and fate of the compound(s).

By varying enough parameter values in a model it is possible to fit almost any observed data; this negates the usefulness of the model for any purpose other than empirical description. Therefore, it is important that a philosophy of model formulation and parameterization be established in order to guarantee that models will be applicable and defensible in assessing the impacts of toxic chemicals.

All actions of living organisms are influenced to some degree by probabilistic considerations. Furthermore, the distribution of substances in nature, whether in a physical sink or in the tissue of living organisms, is not uniform. It varies both temporally and spatially, within a range of extremes, often with a distribution that is far more normal in the Gaussian sense. This distribution is a central problem for systems ecology.

The question of stochasticity in the behavioral action of individual organisms can be handled reasonably well by averaging, provided a large number of individuals within the scope of the system modeled and the probability distributions are monotonic. For example, questions of the timing of feeding, reproducing, defecating, etc., by individuals in pond A as opposed to those same species in pond B are unimportant when the model summarizes the net result of thousands of such individual decisions. The realized average specific rate of growth and ingestion is an adequate predictor.

Different analytical techniques must be utilized when the behavior of small numbers of individuals is to be simulated or the spatial and temporal patterns produce non-monotonic probability distributions. One important variable is the range. The toxic effect can be expected to be related to the extremes as well as to the chronic mean value, often in a complicated nonlinear manner. The model must have built into it the capability of simulating such different temporal and spatial variations in concentration in order that "best" and "worst" case simulation estimates can be obtained. Considerable research effort should be devoted to ecological modeling with this general best and worst case scheme or goal.

This inherent variability in biological systems affects the loads of toxic chemicals that organisms may contain. For example, in the James River many adult bluefish have high concentrations of Kepone, while some have very low concentrations because they have just recently migrated into the estuary. This bimodality has to be considered in monitoring body loads. It also should be considered in predicting the body loads using mathematical models.

The variability of bioaccumulation can be incorporated into predictive models in at least two ways at the present time. Mean parameter values can be used to obtain mean values of toxicants and distributional statistics can be superimposed on these (Schofield and Krutchkoff 1974). Different values of individual parameters can be used with a Monte Carlo technique to obtain repetitive simulations and the output can be summarized in terms of best, worst, mean and standard deviation estimates. In either case, it is necessary to have at least minimal statistics for the important parameters.

4.4.2 Validity and Reliability of Ecosystem Models

Biological mediation of the transport and fate of toxicants can only be modeled through the use of mathematical descriptions that connect chemical and physical properties of the toxicant to observable properties of ecosystems. The resulting models will inevitably contain a mix of probabilistic correlations, process relationships, and system-level interactions. Experimental studies involving toxicants must include a parallel characterization of the environmental processes that control the expression of the phenomenon in real systems, including those factors that govern the dynamics of biotic components.

The major area where research is imperative includes research that associates ecosystem properties with toxicant dynamics. Properties that indicate the ability of systems to degrade toxicants cannot be generalized until the environmental determinants of microbial activity are discovered. At present there is little rationale for predicting gross population sizes, the proportional representation within the population of those organisms that will actively degrade a toxicant, the time required for the microbiota to adapt to the toxicant, or the net degradation rate that will develop over time in an ecosystem setting. In many cases toxicant processes may be intimately associated with normal energy processing within the community. This suggests that research relating gross primary and secondary productivity, respiratory metabolic activity, and energy flow through the community to toxicant dynamics would be important.

In a more general sense, the ways in which a toxicant can modify the "fate processes" through its toxic properties per se are still largely unknown. Microbiological studies using a toxicant as a sole carbon source carry the hidden implication that the toxicant is itself a significant energy source for the system. Alternative plausible assumptions include the possibility that degradation of the toxicant constitutes a simple drain on the metabolic capability of the community or that it is an energy source whose use pattern will depend on the availability of more readily degradable substrates. Research is needed to determine, as a function of the physical-chemical properties of the toxicant, which of these assumptions is most likely to hold for important classes of real ecosystems. More importantly, both true "toxic effects" and the introduction of exotic energy sources may distort normal ecosystem functioning by differential effects within component subsystems.

For example, the microbial community that normally functions in recycling of inorganic nutrients could be modified either by toxic effects or by competition with toxicant degraders. In an aquatic system is it easy to imagine a chain of causation leading to a decrease in productivity, a consequent modification of the pH regime, and a diminution of the rate of base-catalyzed hydrolytic decomposition of the toxicant. This causal chain would give a positive feedback loop that could systematically destroy the system. Fortunately, real ecosystems are buffered against these processes by their structural complexity and by high diversities and niche overlaps that provide redundancies in functional components. However, research into the tolerable levels of functional simplication, as determined by the magnitude of loading or the properties of toxicants, is at present virtually non-existent.

Research that associates ecosystem properties with toxicant transport is also required. There are several classes of biologically-mediated transport of toxicants that have a major impact on the fate of the material. In aquatic and marine systems, filter-feeding organisms can capture large quantities of toxicants sorbed to particulate materials and vastly accelerate the rate of incorporation of toxicants into the sediment phase of the system over the rate suggested by simply physical principles. Furthermore, bioturbation of aquatic sediments and soil turnover by terrestrial invertebrates are the prime determinants of the magnitude of total capture of a toxicant within the soil/sediment phase of many real systems. Although the degree to which toxicants will be entrained in these processes can perhaps be predicted from the sorptive properties of the toxicant, the magnitude of entraining flows and the bulk of materials involved (i.e., depth of mixed layers) need further research at both the descriptive and functional levels of ecosystem ecology.

Some types of biologic transport may have only minor impact on the "fate" of the compound, but nevertheless are important in that they amplify the toxic impact of the material and shunt the toxicant into regions or components that have not been directly contaminated by physical transport processes. Transport of toxicants across phase boundaries, through geographic barriers, and among subsystems within a single ecosystem are important types of food chain transport that can be accomodated only in the context of ecosystem analysis.

Unfortunately, the general significance of the phenomena epitomized by the consumption of DDT-contaminated fishes by bird life, the direct transport of Kepone to crab populations in non-contaminated areas by bluefish migration, and the advection of toxicants into detrital food chains via uptake by higher plants, cannot be determined from anecdotal information alone. Research is needed to determine the minimum spatial scale required to accurately portray ecosystem effects and the ecosystem properties that would impart a plausible descriptive capacity to models that include toxicant movement through food chains. Although some pertinent ecological information is certainly available such as home ranges and migratory ranges for animal species, toxicant body burdens as a function of sexual differences and life-history stages and other large-scale integrative effects have not yet been systematically incorporated in models that are accessible to small-scale testing and validation.

4.4.3 Validation of Ecosystem Models

A model that is theoretically sound and assembled in a way that allows for extrapolation does not utilize arbitrary "calibration factors" or correlations extrapolated beyond their range of observation. Questions of reliability and validity can be reduced to a series of technical assessments of the assumptions and process designations used in constructing the model. These assumptions usually include several levels of integration ranging from molecular chemistry to ecosystems. Validation requires testing at the several levels of integration. The objective of validation is to attempt to test the plausibility and robustness of the model's assumptions. Although all assumptions can be tested in concert at the highest level of resolution represented in the model, a simple test at this level will fail to identify those assumptions that are causing discrepancies.

The assumptions at the lowest level of integration are usually the most accessible to laboratory experimentation, while ecosystem effects can only be validated through critical monitoring and case studies. However, it is important to initially validate at lower levels of integration and proceed toward field validation in a logical series of investigations. In this way, the high-level assumptions can be reduced to constant values, and the particular set of assumptions to be tested in each investigation can be clearly specified.

Time and space are probably interchangeable entities in ecological models in that they both can be expressed as probability distributions for given ecological interactions. Because of this, it is not possible to restrict the spatial dimension of an experimental arena without altering the frequency of interactive events. This is particularly true with macroscopic plants and animals. Many of the stability characteristics of ecological communities result from the co-evolution and convergence of these same probability distributions. Abundant research with predation and inter-specific competition has demonstrated the validity of these observations (Huffaker 1958; Luckinbill 1973).

It is essential, therefore, to develop a hierarchical experimental design to determine the validity of predictive models that range from simple laboratory estimation of parameters to full scale hypothesis testing at the ecosystem level. Parameters whose values are determined primarily by physical and chemical processes should maintain their integrity through the hierarchy. Parameters whose values are products of ecological interactions should demonstrate convergence as the influence of scale is diminished.

Experiments designed to determine the "calibration for scale" must involve a degree of environmental regulation in order to buffer the experimental system from uncontrolled exogenous influences. These larger scale experiments will involve online monitoring, pulsation experiments in series, and rapid assessments of errors for model adaptation.

The hierarchy involves estimates of rate coefficients from reactions involving isolated processes. First generation models then serve as complex hypotheses which then can be challenged through controlled microcosm experimentation. Differences between expected and observed behaviors are then utilized to modify the models. Outdoor mesocosms (farm ponds, experimental streams, isolated salt marshes, and field plots) can then be utilized to test the validity and importance of ecological interactions. This step will require careful selection of the experimental unit and/or partial environmental regulation. Finally, large scale episodic events like the Kepone incident can be utilized to test hypotheses (models) at the regional level. Environmental regulation at this scale will not be feasible. Continuous environmental monitoring programs will be necessary to prevent "drift" of the environment over time.

Although particular tests can only be specified given a particular model, a general scheme for organizing research programs can at least be outlined. Program offices and granting agencies should consider the propriety of funding particular projects as a function of the degree to which necessary antecedent projects have been initiated. Furthermore, a process of integration of the efforts at various levels should be developed.

1. Laboratory studies: given a sound relationship between environmental variables and toxicant properties, the statistical noise and parameter values of the relationships can be determined through direct laboratory studies.

2. Microcosm studies: given a set of validated unit process relationships, the assumptions used to assemble the units can be tested in the context of a controlled, reduced set of environmental variables. This test series also examines one kind of completeness of the unit processes.

3. Mesocosm studies: in larger scale tests (e.g. experimental ponds and channels), the assumptions used to account for stochastic variation in environmental functions can be assessed. At this level, ecological ecosystem variables can be described (e.g., bioturbation of bottom sediments, population densities), but their dynamics cannot be tested.

4. Case studies: actual case studies serve to test model assumptions concerning ecosystem-level effects of biological forcing functions on transport and tranformation.

Note that the spatial scale of the models and the level of integration of the assumptions under investigation continually expand in the test series. It is important that the series be executed in the order specified because each level of assumptions must be tested in a context that allows assumptions at higher levels to be reduced to constant values. It is important that the same model be tested throughout the validation series, i.e., the assumptions used in assembling "sub-models" must also be subjected to critical examination.

4.4.4 Microcosms

In a broad sense, a microcosm is a laboratory approach to the study of environmental processes as they occur in natural systems. Microcosms are capable of simulating only specific situations or portions of the environment. To be useful a microcosm should incorporate the important components and processes of natural systems and should be studied under controlled laboratory conditions to yield reproducible results.

Because of variations in species composition commonly experienced in microcosm studies, process oriented measurements appear to be the best methods for characterizing and defining parameters of microcosms. Production to respiration ratios, nitrogen fixation, and heterotrophic activity can show good consistency from one microcosm study to another. As a result, microcosms can be useful tools for assessing some fate and transport processes. The relatively small size of microcosms permits excellent versatility in determining the effects of common environmental parameters. The ability to test for these effects will lead to definition of parameter limits and validation of the process analyzed.

Microcosms, as laboratory systems, do possess some inherent limitations. Their small size is desirable for reproducibility and versatility, but makes microcosms poor for simulations of total ecosystems. Also, microcosms are not capable of simulating fate and transport processes for larger animals whose biomasses are generally greater than zooplankton or soil/sediment invertebrates. They are, however, useful in performing fate studies with higher plants.

Synthetic or gnotobiotic microcosms are limited since complex biological interactions are minimized and only species readily cultivated in the laboratory are used. Naturally derived microcosms are affected by scaling factors, lack of consistency in the inocula, and previous history.

4.4.5 Mathematical and Physical Model Recommendations

Biological fate models that are to be used in assessing site-specific impacts should be capable of representing separate segments simultaneously so that biological heterogeneity can be taken into consideration. Techniques for representing final spatial resolution and/or automatically connecting adjacent spatial segments should be adapted and refined for use in biological fate models.

Because a complete mass balance study is a major undertaking, criteria should be established for deciding when such a study is necessary and when measurement of only selected transport pathways and sinks may be substituted.

Models should be formulated so that all parameters have physical significance and are subject to estimation using laboratory or field techniques. So-called "free parameters" that do not have physical significance and that are adjusted during the calibration of the model in order to obtain a better fit to data should not be used. To do so would result in the validity of the model being subject to challenge in an adversary proceeding. All parameter values should be documented in such a way that their validity can be established. Where applicable, ranges of values should be given so that constraints can be placed on the limits of parameters.

Predictive models should provide information on variability of toxicant loads in the biota appropriate for assessment purposes. The variability should be utilized in establishing probabilistic confidence intervals for any quantity utilized in a regulatory fashion.

For many classes of toxic substances, the transport and fate dynamics are directly influenced by ecological processes. Existing ecosystem models developed around energy and nutrient dynamics should be modified to "enslave" the associated dynamics of particular toxic substances. Existing models should be utilized for which there exist physical analogs amenable to direct, experimental verification.

Case studies should be selected and the hierarchical experimental design implemented to calibrate the quantitative influences of "scale" and to identify the qualitative distortions due to typical ecological interactions. The case studies chosen should have a regional monitoring program already in operation. The Kepone incident in the Chesapeake Bay or the Mirex incident in Lake Ontario are good candidates.

Microcosms, like any simulation of natural processes, should be validated. Validation methods need to be established and tested. Presently available validation techniques which should be further tested and applied are:

1. Comparative studies relating microcosm and ecosystem experiments in which the environment is perturbed by a chemical.

2. Calibration with standard reference chemicals for which information is known concerning fate and transport.

3. Development of correlations between the activities of various biological processes of natural systems and microcosms.

4. Mathematical modeling of the microcosms should be undertaken. Efforts must be directed toward obtaining verified, quantitative measures of the various physical, chemical and biological parameters (e.g., chemical hydrolysis, photolysis, biodegradation and sorption-desorption) from microcosm studies.

5. Design features of microcosms should be carefully examined and optimized prior to use for fate assessment. Scaling factors, substratum to air or water rations, turnover of air or water, sensitivity to sampling variation in the inocula, nutrient cycling rates, and long-term stability should be investigated experimentally.

4.5 MONITORING

4.5.1 Use of Biological Monitors as Transport and Fate Indicators

There are a number of chemicals which have been found to be long lived in the environment and are scarcely affected by chemical or biological transformation. These chemicals may be more easily handled than those compounds which are greatly transformed as they pass through the environment. The analysis of key organisms could provide positive indications for a large number of chemicals which enter the environment.

Surveys can be run using indigenous species, such as has been done in Mussel Watch (Golberg et al. 1978), looking for specific chemicals. If the chemical is found, one can work backwards and identify the pathways of these chemicals through the environment. If pathways are hypothesized, they could be studied using introduced biological monitors as concentrators of the chemical. This method has been shown to be viable by placing mussels in baskets along a pollution gradient and retrieving them after a specified period of time for tissue analysis.

4.5.2 Monitoring for Unknowns

Utilizing state-of-the-art extraction and analysis technologies, Huggett et al. (1979) observed over 400 individual species of halogenated hydrocarbons in oysters from the Chesapeake Bay. Only about a dozen of these compounds have currently been identified and characterized. The majority of organic toxicants moving through ecological pathways are unidentified and uncharacterized. The information is not currently available to structure and initiate productive models for the vast majority of toxic substances.

Early indication of the transport of a new toxic substance can be obtained from time series analyses of organic "finger prints" taken from key organisms associated with transport mechanisms. Further research and regulatory options are retained if similar materials are stored in a specimen bank such that the chemical integrity of the samples are maintained.

The temporal and spatial pattern of a new emerging peak is sufficient evidence to mobilize human and monetary resources. Furthermore, these patterns give direction to the research and sampling efforts required to identify and characterize the unknown. If the indicator organisms are chosen correctly, the major transport mechanism associated with specific ecosystems will be monitored for the passage of new toxicants. This approach will not preempt the release of toxic substances, but will reduce the response time of the regulatory agency. In addition, the limited available human and monetary resources can be allocated in a most effective fashion.

4.5.3 The Use of Chemical Surrogates in Transport and Fate

The vast majority of toxic chemicals are proving to be organic in nature. Analysis for these chemicals is typically very expensive, especially when dealing with a large scale monitoring or survey program designed to define the transport and fate of these chemicals in the environment. One alternative is to use a more easily analyzed chemical surrogate which has been shown to function as a tracer for the chemical of interest.

There are several possibilities of tags on the actual compound of interest or an environmental tag useful on the process involved. Radioactive tracers are an obvious example of the first type. A similar but less common example is the possibility of following the path of halogenated hydrocarbons by analyzing for the halogen, rather then the compound itself.

The use of an easily analyzed chemical species, which can be shown to follow the chemical of interest in a particular environment, is also a possibility. It has been shown, for example, in Narragansett Bay, R. I., that body burdens of nickel can be directly correlated with the level of total hydrocarbon in the tissue of Mytilus edulis. Since the analysis of an organism for metals can be one or two orders of magnitude lower in cost than for hydrocarbons, the use of such a surrogate may be a necessity as well as an attractive alternative. In a large mapping program, a surrogate could be determined and used as the major tag. A subset of samples could also be analyzed periodically for the chemical of interest to reconfirm validity of the technique.

4.5.4 Monitoring Recommendations

EPA should support further research in the use of biological organisms as concentrators for the study of transport and fate of various chemicals in the environment. For example, many organics are dumped into upper Narragansett

Bay and their movement through the bay system could be followed through the analysis of mussels placed in specific patterns throughout the bay. Software should be developed to allow sufficient analysis of existing mussel watch data to evaluate the application of such a monitoring program to the transport and fate of chemicals in the environment.

EPA should continue to support the development of a monitoring program for "unknowns" and an associated specimen bank. Specific attention should be directed toward indicator organisms that reflect the major pathways of biologic transport. Particular emphasis should be given to the development of analytical techniques for pattern identification with time series data.

A research effort should be initiated to determine the viability of using comparatively easily analyzed materials as surrogates for the organic toxic chemicals of interest. For example, the data resulting from the first three years of Mussel Watch could be run through statistical analysis to see if any of the five metals analyzed could be used as surrogates for any of the organics also analyzed in the same samples. Large scale survey studies of the transport and fate of chemicals which are prohibitively expensive due to the high cost of analysis can become feasible if appropriate surrogates are available.

4.6 METHODOLOGIES

4.6.1 Software for Analyzing Monitoring Data

A number of multivariate techniques exist for discerning patterns of occurrence and for identification of anomalous occurences (Park 1975). These include cluster analysis, factor analysis, ordination, multiple regression, and discriminant analysis. Such techniques would be quite useful in analyzing Mussel Watch data on "unknown" compounds. These analyses would provide insight into efficient allocations of human and monetary resources devoted to the monitoring activity. In addition, they would assist in the identification of surrogate compounds.

Multivariate analytical strategies have been utilized in geological and ecological investigations for years (Parks 1966; McCammon 1978; Park 1974; Allen and Koonce 1974), and are appropriate for objectively and systematically processing large quantities of data on body loads. They reduce an almost incomprehensible array of data matrices to indices and graphic patterns that can be readily interpreted.

4.6.2 Speciation of Metals

Research on trace metals in the aquatic environment often centers around laboratory experiments utilizing the metal in the inorganic form. Results from these experiments are then extrapolated to the real world via mathematical models. A major pitfall in this logic is that the metals may not be in the inorganic form in the environment due to chelation or complexation by organic substances. These organic forms can in turn be more or less biologically available than the inorganic ones.

One reason the organo-metallic species have been slighted is because of the analytical difficulty in identifying and quantifying the complexes. Commonly used methods for analyzing metals such as atomic absorption spectrophotometry or activation analysis do not differentiate between chemical species unless special extraction techniques are employed, and even then the state-of-the-art is marginal.

New analytical methods to identify speciation are being developed. An example is the coupling of high pressure liquid chromatography with Graphite Furnace Atomic Absorption. Research should be funded that develops new techniques for identifying and experimenting with the transport of metallo-organic compounds. Without this experimentation work will continue with inorganic metals as surrogates of real world complexes which could result in errors in estimating biological effects, biological transformations, and biological transport of trace metals.

4.6.3 Analtyical Techniques

Toxic compounds which enter the environment from anthropogenic sources are supposedly controlled via the permit system. When a permit is issued for discharge, there is an implied assumption that the discharge will be monitored to assure compliance. For many of the substances entering the environment, analytical methods to determine the compound at environmental levels (i.e., µg/g, µg/g) in water, tissue, and sediments do not exist. For many substances which are permitted, the ability to monitor is hampered by inadequate manpower and instrumentation at both state and federal levels when analytical methodologies exist. Therefore, the role of organisms in transport and transformation of these substances is inadequately known for natural field situations.

The modeler must incorporate into the mathematical expressions, which approximate the real world, those pathways which will affect the distribution of the substance. If better monitoring systems were in effect for anthropogenic compounds in the environment, including the biotic compartment, then these data and the resulting conclusions could be incorporated into future models.

4.6.4 Exposure Determination

Prediction of risk requires knowledge of: the chemical and physical form and the biological availability of the toxic substance, the total amount incorporated by the receptor, the rate and pathway of incorporation, the frequency and duration of exposure, the time intervals between the periods of exposure, and an understanding of the life history and population characteristics of the organism involved. In the past, aggregate statistics on the concentration of substances in soil, water or air medium have been used to evaluate hazards and the above mentioned details have been lacking.

The aggregate statistic approach is inadequate because the process of bioaccumulation and biotransformation can markedly alter the experiences or effective concentration of the substance. Another factor is that normal population processes produce variations in uptake and accumulation rates as a function of seasonality, diurnal rhythms, genetic state of the population, and stage of life history development. Also, the repair and recovery processes operate during intervals between periods of incorporation and the adaptive, avoidance or exclusion responses can function as behavioral alternatives during periods of exposure to toxic substances.

4.6.5 Methodology Recommendations

Generally accepted multivariate analytical strategies should be employed in the analysis of monitoring data (like Mussel Watch) so that patterns, trends, and anomalous occurrences can be readily perceived.

Work should commence immediately to examine existing analytical techniques for analyzing metallo-organics and their applicability for utilization in microsm-mesocosm-megacosm research. These metallic species must then be incorporated into existing or new mathematical models on the fate and transport of trace metals.

Analytical techniques must be developed to allow better monitoring of existing systems into which anthropogenic substances are discharged. The discharges chosen should be those which contain compounds with a wide range of organic structures. Techniques should be developed which allow extraction and analyses of multiple substrates - i.e. animal tissues, plant tissues, sediments.

The concept of exposure must be expanded to include active ecological and behavioral responses of organisms to the presence of toxic substances. Factors like those listed above should be evaluated and incorporated into risk assessment models.

4.7 EXISTING DATA REQUIREMENTS

4.7.1 A General Overview of the Types of Information Currently Reviewed by EPA in Considering the Registration of Pesticides in the Area of Fate and Transport

EPA reviews a number of physical and chemical parameters including melting point, boiling point, water solubility, solubility in organic solvents, vapor and quantity of impurities, octanol/water partition coefficient, explosiveness, miscibility, corrosive characteristics, specific gravity, and pH.

Other data reviewed in the area of environmental chemistry include:

A. Physicochemical Degradation

1. Hydrolysis (at different pH values)
2. Photolysis (soil surfaces and aqueous)
   Sufficient data are required for these studies so that rate constants can be calculated.

B. Metabolism

1. Plant (rotational crop uptake)
   These studies require the identification of the nature of plant residues in mature crops.

2. Soil (aerobic and anaerobic)
   These tests are qualitative in nature and emphasize the nature of the degradation products rather than their amounts. However, studies outlined under Section D require field persistence data of parent compound and significant degradation products.

3. Aquatic (aerobic and anaerobic)

4. Bird (poultry)

5. Microbial

   a. Effects of pesticides on microbes

      These studies can involve either the effects on microbial function or microbial populations. Some effects cannot be measured directly and population studies may be the only recourse. Data obtained include O_2 consumption, CO_2 evolution, nitrogen cycle reactions, and measurement of enzyme activity for dehydrogenase and phosphatase. When the functional approach is used, data on the effects of nitrogen fixation, nitrification and degradation of cellulose, starch and proteins may be utilized.

   b. Effects of microbes on pesticides

      Effects are determined on pure or mixed culture populations of representative microorganisms from soil or water including free-living nitrogen fixing bacteria and blue-green algae such as Czatobocler, Clostridium, Nostoc, and nitrofiers such as Nitrosomanos and Nitrobacter. For cellulose, starch, pectin and similar substrates, selected soil bacteria, actinomyses, and molds should be utilized.

6. Activated Sludge

C. Mobility

Column leaching studies and/or soil TLC and/or adsorption/desorption studies are done on solid and sediment.

D. Persistence Under Field Use Condition

   1. Soil

   2. Sediment

   3. Water

   4. Specialized Ecosystems

E. Accumulation

   1. Irrigated Crops

   2. Fish

      a. Flow thru systems

      b. Static laboratory systems containing treated soil (sediment)

   3. Field Study

Frequently the conduct of the above-mentioned studies is facilitated by the use of radio-labeled compounds with routine mass balance for laboratory type studies. Identification of major degradation products is routinely performed either by co-chromatography with model compounds and/or mass spectrometric confirmation. The most recent statement of EPA's need for data can be found in the Federal Register of July 10, 1978, Part III, Registration of Pesticides in the United States: Proposed Guideline for Registering Pesticides in the United States.

Additional information required of pesticides for which tolerances on food are established include the decline of residues versus time between treatment and harvest and metabolism in plants and rats (or other animals). These data requirements in support of a pesticide tolerance are provided for by certain parts of the Federal Food, Drug and Cosmetic Act.

The exact type and quantity of data required of a pesticide registrant is dependent on the proposed pattern(s) of use. More data are required for pesticides to be used on or near water than for certain limited terrestrial uses.

4.7.2 A General Overview of the Types of Information to be Reviewed for Toxic Substances

The chemicals that will have to be regulated by the Office of Toxic Substances (OTS) under TSCA fall into the categories of new chemicals (Section 5) and existing chemicals (Section 4). In general, the premanufacturing notification form for new chemicals will include provisions for the informational elements listed for pesticides (except for those marked as "not applicable" (n/a)). Since Section 5 is not a set of requirements but merely serves as a guideline, it is problematical as to how much of these data will actually be provided by the potential manufacturer. Additional information can be obtained through court action under Section 5e only if EPA can make a case that it is essential to make a risk assessment.

Test protocols for existing chemicals are going to be published as requirements. However, of the 70,000 chemicals already in commerce, only a few will be selected annually for inspection. This process begins with the preparation of a dossier on each of the selected chemicals or chemical classes after which data deficiencies are noted and manufacturers notified that certain critical testing has to be performed to correct these deficiencies. It is estimated that EPA will consider 50-150 such chemical/classes per year. So far, a review of about 20 dossiers indicates that most contained essential physical/chemical data but had little persistence data (none photochemical), and none contained much in the way of ecological effects data except for short term (acute) toxicity data on relatively few species.

Thus, ball park figures indicate that the score is:

- Physical/chemical data - 70 percent
- Persistence data - 5 percent
- Ecological data - 15 percent
- Photochemical - 0 percent

Since EPA Section 5 test guidelines are only in draft form and Section 4 test rules are just being formulated, it is not yet possible to spell out the complete spectrum of testing guidelines and requirements that the Office of Toxic Substances will eventually develop. TSCA mandates that all test protocols be reviewed annually so they will always be amenable to changes as required.

4.7.3 Parameters Required by PEST Model (Park et al. 1978)

Solution

SOLS - solubility of the solid
EK - dissolution constant

Adsorption-Desorption

K1 - rate constant for adsorption
K2 - rate constant for desorption
MO - limiting number of moles adsorbed per grain

Volatilization

H^* - Henry's law constant
P_A - Partial pressure of solute

k_L - liquid mass transfer coefficient
k_G - gas mass transfer coefficient
p_{AG} - partial pressure of A at film-gas interface
p_{Ai} - partial pressure of A at film-liquid interface

Chemical Degradation

KO - uncatalyzed rate constant
KH - hydrogen ion constant
KHO - hydroxide ion constant
KHA - rate constant for hydrolysis by the i^{th} acid
KHB - rate constant for hydrolysis by the i^{th} base
HA - concentration of the i^{th} acid
HB - concentration of the i^{th} base
NA - number of acids
NB - number of bases
OPTPH - optimum value of pH
SIGPHA - parameters used to "shape" reduction
SIGPHB - factors for non-optimum pH conditions
KSI - quantum yield of reaction considered
EPT - molar absorptivity of TOM at particular wave length

Excretion

KEXFAT - proportion of TOM excreted under starvation conditions
KEXPRT - proportion of TOM excreted under normal maintenance

Defecation

E - proportion of TOM not assimilated

Microbial Metabolism

AA - four regression coefficients of second-order fit of growth and mortality to TOM concentrations

MUO - growth rate coefficient in absence of TOM

KDO - mortality coefficient in absence of TOM

4.7.3.1 Data/Model Recommendation

The information required to initiate and utilize an ecosystem model like PEST should be compared with the existing requirements for data under EPA rules and regulations. A strategy for addressing the discrepencies should be immediately addressed. Otherwise, even existing models will not be available for routine risk assessment.

The Biota Group participants are listed in Table 4-1.

TABLE 4-1. BIOTA GROUP PARTICIPANTS

Non-Agency Participants

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5.0 EXPOSURE ASSESSMENT AND MODELING IN TRANSPORT AND FATE RESEARCH

5.1 INTRODUCTION

The need for multimedia models of the transport and fate of toxic chemicals in the environment has been widely recognized only in the past ten years. Prior to the late 1960's, comprehensive, detailed models of environmental transport and fate had been developed primarily only for radionuclides. Models for restricted applications such as dispersion models for air pollutants had also been developed prior to this date. Other relevant studies conducted at that period fall into the following categories:

(1) Physical transport models for commonly recognized wastes;

(2) Empirical studies of transfer processes such as soil erosion;

(3) Specific studies of individual problems such as pesticide residue dynamics and occupational health exposures.

The development of physical transport models for oxygen-demanding wastes was begun in the 1950's and has continued to serve as the scientific base for current efforts in this area. These models were important precusors of present-day exposure models, but until recently no attention has been given to the application of these models to wastes other than domestic, municipal, and industrial sewage. During the same period, empirical methods for estimating soil erosion rates such as the "Universal Soil Loss Equation" were developed as numerical aids for field extension agents in attempts to improve erosion control. These methods were based on commonsense understanding of the major mechanisms behind material loss and transport, but were largely restricted to specific sites such as plowed agricultural plots and did not connect transport to exposure in any real sense. Finally, specific issues of pesticides and occupational health exposures were considered as isolated problems that could be analyzed without close analytical attention to multimedia transport.

The discovery in the late 1960's that DDT is transformed into DDE and causes important environmental effects away from the site of application was perhaps the first stimulus for a systematic study of the transport and fate of toxic substances. The discovery of the methylation of inorganic mercury focused concern on the linkage between biological and chemical transformations. It was also recognized at that time that combinations of pollutants in one medium could have total impact greater than the sum of the impacts of each individual pollutant (e.g., photochemical smog). These observations further emphasized the need for complete assessments of pollutant transport and transformation.

Prior to the mid-1970's, most exposure models for toxic substances were developed on an ad hoc basis for application to specific pollutants which were known or suspected to be causing adverse effects. In most such cases the observed effects dominated discussion of the problem and thus guided the formulation and development of the exposure models. Only in very recent years has the scientific community begun to develop a general methodology for multimedia assessment of exposure to toxic substances which is independent of immediate concerns with effects. The concepts of "materials balance" (Caltech 1978) and "critical pathways" (Friedlander et al. 1970) have been recently introduced into assessment of exposure to toxic substances, and are now being employed as currently accepted techniques.

Some of the earliest models of the environmental distribution of toxic chemicals were based upon knowledge derived from models formulated for radionuclides (for example, see Woodwell et al. 1971). Throughout the period of development of models for toxic substances, work has continued on models of the transport, distribution, and fate of radionuclides, and these models are still much better developed than those for other toxic substances (for a summary of the available models see section 5.5.1 below). We expect that the development and improvement of comprehensive techniques for exposure modeling of toxic chemicals will continue to benefit from experience gained in studies of radionuclides. In addition, multimedia studies will depend on the development of improved methods for modeling distribution and transport of chemicals in a single medium. These methods are discussed in other chapters in this report.

The overall emphasis in this chapter is on the modeling of exposure levels across more than one environmental medium. Current multimedia studies are described in detail in sections 5.5 through 5.11 of this chapter. The small number of available studies, combined with the discussion above, should be a clear indication to the reader that the evolution of exposure modeling efforts is at a very early stage and that historical experience provides only a broad sense of the scope of effort required.

5.2 OBJECTIVES OF MULTIMEDIA MODELS

The usual purpose of constructing an exposure model is to derive predictions of the exposure[1] of target populations to a chemical resulting from various types of use of release into the environment. Most models are developed in a regulatory context, to estimate whether or not specific uses of a chemical will lead to exposures that will cause adverse effects on target populations. For this purpose, it is often necessary to construct models that will establish cause-and-effect relationships between specific releases of chemicals into the environment and resulting exposures to sensitive populations.

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[1] The term "exposure" has been used in a number of different ways. For the definition used in this chapter see Section 5.9 below.

Multimedia models are necessary when a chemical either is released into more than one environmental medium, or is transferred from one medium to another after release, resulting in multimedia exposure. Multimedia pollutants are inherently more difficult to study than single-medium pollutants because transfer coefficients are often difficult to measure and are very difficult to calculate theoretically. In cases where a pollutant has multiple sources, it is often very difficult to identify the critical pathways linking the most important exposures with specific sources.

Multimedia exposure models for toxic substances vary considerably in complexity ranging from simple empirical relationships or arithmetic exercises to complex computer models with many adjustable parameters. To avoid wasting resources on inappropriate levels of study or of regulatory control, it is important to match the scale of the model to the importance of the problem and to the amount of data available. In many cases it is desirable to use an iterative approach, in which successively more complex models are used to define the potential significance of a pollutant, to make rough estimates of likely exposures, to design a monitoring program to measure actual concentrations in the environment, and to make a detailed analysis of critical pathways. When a model predicts that hazardous exposure concentrations are likely to occur, it is very desirable to conduct sensitivity studies to determine whether the predicted exposure levels are strongly dependent on assumptions made about source strengths or transfer coefficients.

Because estimates of exposure derived from modeling exercises are often uncertain, it is desirable to test the model at all stages of development against field measurements. The usual approach is to follow an iterative pattern in relating the model exercises to field measurements. Usually, the first indication of the relative importance of the variables is apparent in bodies of observational data. The next step is to construct a model on the basis of either intuition or a deterministic physical relationship that reflects the trends seen in the data. The model is then applied to the range of conditions in the data base, and uncertainties as to the adequacy of the model or of the completeness of the data base become evident. Questions which arise can usually be answered only through further measurement programs. In this way a model appropriate to the specific pollutant is developed.

5.3 CHARACTERISTICS OF MULTIMEDIA MODELS

The basic structure of an exposure model is illustrated in Figure 5-1. The system is initially characterized by the initial distribution of the chemical and by the characteristics of the chemical and of each of the media which control the behavior of the chemical within and between them. The system is driven by the source terms, which describe the rates of release of the chemical as functions of space and time. These input data are processed according to the logic specified by the modeler and are used to derive the output data, which are predicted concentrations, and the chemical as functions of space and time. In certain cases the model may be "run" backwards, using the observed distribution of the chemical in the environment to derive inferences about the relative importance of different sources.

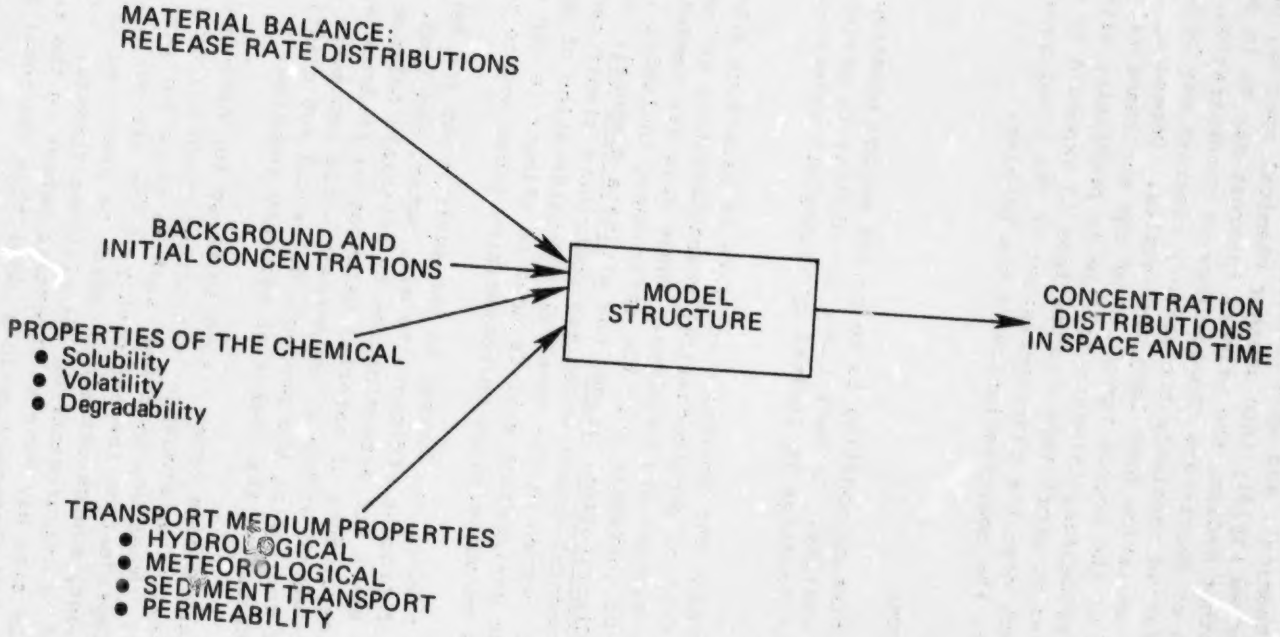
MATERIAL BALANCE:
RELEASE RATE DISTRIBUTIONS
BACKGROUND AND
INITIAL CONCENTRATIONS
PROPERTIES OF THE CHEMICAL
• Solubility
• Volatility
• Degradability
TRANSPORT MEDIUM PROPERTIES
• HYDROLOGICAL
• METEOROLOGICAL
• SEDIMENT TRANSPORT
• PERMEABILITY
MODEL
STRUCTURE
CONCENTRATION
DISTRIBUTIONS
IN SPACE AND TIME

FIGURE 5-1. SCHEMATIC OF THE STRUCTURE OF A DETERMINISTIC MODEL.

The specifications of the model and of its input and output data may vary greatly depending on the characteristics of the chemical and the purposes for which the output data are to be used. For example, the spatial and temporal scales of interest depend on spatial and temporal scales of release, on the lifetime of the chemical, and upon transfer rates. For a short-lived chemical which is transformed rapidly into another chemical species, or transferred rapidly into another medium, the primary interest may be in defining local diffusion scales or short-term fluctuations in concentration. For long-lived or slowly-transferred chemicals the primary interest may be in long-range transport or accumulation over long time-scales. Depending on the characteristics of the source terms and of the environmental transport and transformation processes, interest may lie in predicting either long-term average exposures or short-term fluctuations in exposure to specific sensitive targets. In each case the characteristics of the model should be adapted approximately to the characteristics of the problem.

5.4 SOURCE TERMS

One objective of modeling is to relate source emission data to ambient environmental quality. In many cases the ability to project steady state or dynamic ambient loadings is limited by incomplete understanding of the source terms.

In addressing the transport and fate of hazardous substances in the environment, data on physicochemical characteristics and on discharge rates from specific sources are required. These data are needed for all stages of introduction of chemicals into the environment including losses during production, distribution, usage, and ultimate disposal. Any combination of these environmental source modes may contribute significantly to the total environmental burden of the chemical. Consideration of specific examples of loss into the environment will be used to illustrate the difficulties that may be sometimes encountered in characterizing these source terms.

During production, losses to the environment are determined usually by monitoring of process effluents to air, water, and land. These losses are usually too small for determination by materials balance methods. For chemical processes the closure of material balances on feedstocks, intermediates, or product streams to within a few percent would represent adequate closure for purposes of monitoring the process, but would not quantify the residual or effluent streams to the degree of accuracy required.

Certain source terms - such as those for nitrogen oxides produced by thermal fixation of atmospheric nitrogen - are strongly related to process conditions. Other source terms, such as those for particulate emissions, are strongly dependent on the efficiency of the air pollution control devices. For these reasons, source emissions cannot be predicted in most cases and must be determined by measurements on the effluent streams. Often other factors such as particle size may have an important impact on the transport of the pollutants and characterizations other than the total quantity of effluents are necessary. For example, the distribution of lead emitted into the Los Angeles Basin has been found to be governed by the distribution of the size of lead particles emitted by automobiles .

Many of the early episodes of environmental contamination could be related to stationary and mobile combustion sources or chemical plants. Systematic measurements of effluents from these sources have provided statistical bases for evaluating emissions (U. S. Environmental Protection Agency 1976). These data, although useful for establishing acceptable limits of emissions for maintaining environmental quality, cannot substitute for the site-specific monitoring information needed for purposes of validation of models. The Toxic Substances Control Act (TSCA) should be implemented to limit environmental releases to levels which are estimated by exposure-modeling to constitute "safe" ambient loadings. Source monitoring will continue to be needed to ensure that these emission levels are met or to provide data for validation of models.

Another significant factor in source description relates to the consumer usage of the substance in question. In cases where the principal use of the chemical is dispersive (e.g., pesticides and aerosol propellants), the emission rates can be readily estimated from statistics on production and sales; additional information on geographical distribution of use may need to be inferred from regional marketing data in order to identify regional source terms. Another category of use where widespread dispersal of chemicals into the environment may occur, often in amounts equal to production, is that of additives which may be vaporized or leached from a product during its useful lifetime. A well-publicized case of this type is the vaporization of plasticizers such as phthalates out of consumer plastics. In view of the wide range of formulations of polymer products and the sensitivity of the vaporization rate to both the physical and chemical properties, one can anticipate major problems in obtaining reliable data on losses from all the products that fall into this category.

Models based on the physicochemical properties of the materials could be helpful in providing a framework for correlating losses from products of widely varying shape and composition. Unscheduled use of hazardous substances represents another path which can lead to significant exposures. For example, PCB's which had lost their functional dielectric properties are known to have been used as anti-dusting agents in parking lots or as herbicides along roadways; these are uses never envisaged by the manufacturer. The above examples of losses to the environment during usage constitute a class of fugitive releases which will usually be very difficult to quantify by integrating the spectrum of usages. However, recognition that some fraction of the total production of a chemical does not follow the normal track to eventual disposal may allow conservative estimates of loss to be made.

Ultimate disposal of hazardous compounds should not be confused with sequestering of these compounds in storage or reservoir areas. Understanding the distinction between storage and disposal is a prerequisite to describing the total environmental cycle and multimedia materials balance for the substance. During storage, in the absence of biodegradation, losses to the environment proceed over time and ultimately may result in complete release. In a steady-state economy in the longterm, the net effect of storage in "leaky" dumps is to provide a delay time, of the order of magnitude of the residence time in a dump, between time of disposal and time of release into the environment. The recent incident at Love Canal is an illustration of a delay between the time of disposal of a chemical and its appearance in the environment. The cumulative effect of increasing numbers of hazardous chemical storage areas can be expected to result in more frequent situations of this type. From the point of view of the modeler, temporary sequestering of chemicals in dumps requires the inclusion in the model of compartments with long retention times.

An alternative means of disposal is by thermal degradation by pyrolysis or incineration. In assessing these destruction processes for hazardous waste materials, caution is necessary to insure that trade-offs of one toxic substance for another do not occur. High temperatures during incineration may enhance the loss of volatile metals such as mercury and arsenic, and/or the formation of hazardous organic compounds (e.g., polycyclic aromatic hydrocarbons). These emission streams then become an additional source term associated with the subject compound.

Spills of hazardous substances constitute a generic class of intermittent sources with potential for leading to locally acute exposures. Although spills may account for only a small fraction of the total materials balance, protocols for integrating this source term into exposure modeling should be established.

The goal of source assessment for hazardous substances is to set up material flow diagrams for production through ultimate destruction which will identify all entries into the biosphere and all reservoirs. Research by Nisbet and Sarofim (1972) may serve as an illustration of the value of simple material balances. In that work consideration of the fluxes of PCB's through the environment resulted in identification of river and lake sediment as a reservior for PCB's before field measurements identified the importance of this temporary sink. Materials balances are indeed proving to be a powerful tool in identifying and quantifying important environmental pathways in urban areas (Abrott et al. 1978; Caltech 1978).

Although it is desirable to use mass balances to provide a systematic accounting of the flow of chemicals in the environment, there may be critical pathways to man or other receptors that may involve a very minor use of a chemical. The use of solvents in confined quarters and of chemicals in cosmetics are examples of major pathways to exposure to man which may represent only minor uses of a chemical. Although a number of such pathways are governed by existing legislation, judegment will always be required in anticipating problems associated with specified low volume uses of chemicals. The construction of scenarios (Friedlander et al. 1970) provides a possible mechanism for identifying a few problems that would not be detected by conventional modeling techniques because of the small amounts of chemicals involved. However, there will undoubtedly be incidents, such as the formation of dioxins through the reactions of chlorinated phenols at high temperatures, that will not be predicted by any model.

5.5 MATHEMATICAL MODELS

5.5.1 Available Models for Radiological Assessments

The National Laboratories of the Department of Energy have accumulated experience in the area of radiological assessment and have developed assessment methodologies incorporating transport models and external and internal dosimetry models. The models for radionuclides are assessed in this section in order to provide a starting point for the more complex considerations required for modeling chemical pollutants.

Table 5-1 provides a compilation of codes[2] which may be implemented for assessment of radiological consequences of discharges, routine or accidental, from nuclear power facilities. The table identifies the transport processes and human uptake mechanisms covered by each code. Blank areas in the table occur if the column designation is not applicable to the code as determined from the available documentation. Supplementary information on some codes and descriptions of additional codes for accidental release of radionuclides are available (Winton 1969, 1971, 1974; Strenge et al. 1976).

Figure 5-2 depicts the frequency of occurrence of the computer codes compiled within various environmental transport and dosimetric categories. The figure indicates that the assessment of atmospheric dispersion, external dosimetry and internal dosimetry via inhalation have predominated in the development of radiological assessment computer codes. This emphasis probably reflects the need for such codes in safety evaluation work associated with Preliminary Safety Analysis Reports (PSAR's) in which assessment of radiological consequences of accidental releases is of primary importance.

The incorporation of other pathways of exposure into computer codes for assessing radiological safety has been a fairly recent development and reflects the need for satisfying the current requirements of environmental legislation and the needs of regulatory agencies. Previously, calculations of potential exposures resulting from food chain transport and the subsequent ingestion of food were performed for a few nuclides (e.g., ^{131}I, ^{90}Sr, ^{137}Cs). Computations by hand were usually satisfactory for these cases. This situation changes with the inclusion of a large number of nuclides in the source term and the need to estimate doses resulting from multiple exposure pathways. Nevertheless, fewer than 10 percent of the codes in the review have the capability of estimating aquatic and terrestrial transport processes.

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[2] A "code" in the sense used in this section is the representation of a mathematical model of transport and dispersal of a chemical in computer language. A "code" is equivalent to a "model" in the sense that both incorporate the same information and logic.

TABLE 5-1. A LISTING OF COMPUTER CODES AND THEIR CHARACTERISTICS (A = ACCIDENTAL RELEASE, R = ROUTINE RELEASE) (Based on Hoffman et al. 1977a, 1977b)

CODE	ENVIRONMENTAL TRANSPORT											EXTERNAL DOSIMETRY				INTERNAL DOSIMETRY		REFERENCES
	ATMOSPHERIC	WET DEPOSITION	DRY DEPOSITION	RESUSPENSION	SURFACE WATER	GROUND WATER	SEDIMENTATION	IRRIGATION	TERRESTRIAL FOODS	AQUATIC FOODS	HUMAN DIETARY & BEHAVIOR FACTORS[a]	AIR EXPOSURE	GROUND EXPOSURE	SHORELINE EXPOSURE	WATER EXPOSURE	INHALATION	INGESTION	
ACRA	A											A				A		Stallman & Kam, 1973
ACRA-II	A	A	A									A				A		RSIC, 1974
ADPIC	A R				A R													Lange, 1973
AERIN																A	A	Voilleque, 1970; 1968
AIRDOS	R	R	R						R		R	R	R	R	R	R	R	Moore, 1975
AIREM	R	R	R									R				R		Martin et al., 1974
AISITE II	A R											A R				A R		Blaine and Bramblett, 1964
AQUAMOD					A R		A R			A R								Booth, 1975
ARADS	R																	Plato et al., 1967; 1969
ARCON	A		A															Tveten, 1974
ARMSTRONG AND GLOYNA					A R													Armstrong and Gloyna, 1968
ARRRG					R					R	R			R	R		R	Soldat et al., 1974
ATM	R	R	R	R														Culkowski and Patterson, 1976
CARDOCC					R					R	R						R	Watts, 1976
CEDRIC																A R	A R	Clarke, 1972
CHARAK	A	A																Charak, 1967
CLOUD	A											A				A		Bonzon and Rivard, 1970

F

TABLE 5-1. (Continued)

	ENVIRONMENTAL TRANSPORT											EXTERNAL DOSIMETRY				INTERNAL DOSIMETRY		
CODE	ATMOSPHERIC	WET DEPOSITION	DRY DEPOSITION	RESUSPENSION	SURFACE WATER	GROUND WATER	SEDIMENTATION	IRRIGATION	TERRESTRIAL FOODS	AQUATIC FOODS	HUMAN DIETARY & BEHAVIOR FACTORS^a	AIR EXPOSURE	GROUND EXPOSURE	SHORELINE EXPOSURE	WATER EXPOSURE	INHALATION	INGESTION	REFERENCES
COLHEAT					A R													Daniels et al., 1970
COMRADEX I, II, III	A											A				A		Willis et al., 1970 Specht et al., 1975 Otter and Conners, 1975
CURIE/DOSE THUNDERHEAD	A											A				A		Kenfield et al., 1965
DACRIN	A R															A R		Houston et al., 1974 Strenge, 1975
DIFOUT	A R		A R															Luna and Church, 1969
DOSE B												A R				A R		Ellison and Dunham, 1967
DPRWCR					A R													Ahlstrom and Foote, 1976
DPRWGW						A R												Ahlstrom and Foote, 1976
DUGUID & REEVES						A R												Reeves & Duguid, 1975; Duguid & Reeves, 1976
EERIE	A		A									A				A		MacDonald, 1971
EGAD	R											R						Cooper, 1972
ENGLEMANN AND DAVIS	A R	A R																Engelmann and Davis, 1968
ERGAM												A						Cooper, 1976
ESDORA	A R	A R	A R									A R						Cruz, 1973
EXDOSE	A		A									A						Hendrickson, 1968
EXGAM												A						Steyn & Kim, 1966
EXREM I, II, III												A R	A R	A R	A R			Turner et al., 1968 Turner, 1969 Trubey & Kaye, 1973 Killough & McKay, 1976

TABLE 5-1. (Continued)

CODE	ENVIRONMENTAL TRANSPORT											EXTERNAL DOSIMETRY				INTERNAL DOSIMETRY		
	ATMOSPHERIC	WET DEPOSITION	DRY DEPOSITION	RESUSPENSION	SURFACE WATER	GROUND WATER	SEDIMENTATION	IRRIGATION	TERRESTRIAL FOODS	AQUATIC FOODS	HUMAN DIETARY & BEHAVIOR FACTORS[a]	AIR EXPOSURE	GROUND EXPOSURE	SHORELINE EXPOSURE	WATER EXPOSURE	INHALATION	INGESTION	REFERENCES
FETRA					A R													Onishi et al., 1976
FOOD		R	R					R	R		R						R	Baker et al., 1976
GADOSE/DOSET	A	A	A								A	A				A		Lee et al., 1966
GDOS	R											R						Thykier-Nielson, 1974, Hedemann, 1974
GOGOLAK	R											R						Gogolak, 1973
GRONK	R	R	R						R		R	R				R	R	Soldat et al., 1974
HEFFTER ET AL	A R	A R	A R															Heffter et al., 1975
HERMES	R	R	R		R	R	R	R	R	R	R	R	R	R	R	R	R	Fletcher & Dotson 1971, Soldat, 1971
INDOS I, II, III																A R	A R	Killough & Rohwer, 1974
INDOS 2	A R	A R	A R													A R		Thykier-Nielsen, 1974
INHEC	A R											A R				A R		Mackay & Ely, 1974
INREM, INREM II																A R	A R	Turner et al., 1968 Killough et al., 1975; Killough et al., 1977
ISOLA II	R											R						Hubschmann & Nagel, 1975
KRONIC	R											R						Strenge & Watson, 1973
LANES	A R	A R	A R													A R		Lanes, 1964
MESODIF	A R																	Start & Wendall, 1974
METEO-1	A R	A R	A R															Veverka et al., 1975
MILLS ET AL	A R		A R	A R														Mills et al., 1974
MO142	A											A				A		Eckert, 1964
MUNDO	A		A								A	A				A		Heller et al., 1967

TABLE 5-1. (Continued)

	ENVIRONMENTAL TRANSPORT											EXTERNAL DOSIMETRY				INTERNAL DOSIMETRY		
CODE	ATMOSPHERIC	WET DEPOSITION	DRY DEPOSITION	RESUSPENSION	SURFACE WATER	GROUND WATER	SEDIMENTATION	IRRIGATION	TERRESTRIAL FOODS	AQUATIC FOODS	HUMAN DIETARY & BEHAVIOR FACTORS[a]	AIR EXPOSURE	GROUND EXPOSURE	SHORELINE EXPOSURE	WATER EXPOSURE	INHALATION	INGESTION	REFERENCES
NOWICKI	R	R	R									R				R		Nowicki, 1975
NUBE	A	A	A									A				A		Alonso, 1965
NURSE-1	A		A									A	A			A		Couchman et al., 1964
NUS																A R	A R	Kim, 1963
PLUME	A											A				A		Binford et al., 1968
PUDEQ																A[b]		Houston and Heid, 1975
RACER	A											A						Strenge et al., 1971
RADOS	A																	Cooper, 1967
RADS	A																	Plato et al., 1967, 1969
REEVES ET AL	R		R															Reeves et al., 1972
RELISII	A																	Binford et al., 1970
RISC	A	A	A															Anno et al., 1963
RSAC	A R	A R	A R									A R	A R			A R		Coates & Horton, 1966 Richardson, 1968
RSAC-2	A R	A R	A R									A R	A R			A R		Wenzel, 1974
RUBY												R				R		Boone et al., 1975
SATO ET AL	R											R						Sato et al., 1968
SEP	A R																	Sagendorf, 1974
SERATRA					A R													Onishi et al., 1976
SHIH & GLOYNA					A R													Shih and Gloyna, 1967
STAREL	R																	Binford et al., 1970

TABLE 5-1. (Continued)

CODE	ENVIRONMENTAL TRANSPORT										HUMAN DIETARY & BEHAVIOR FACTORS[a]	EXTERNAL DOSIMETRY				INTERNAL DOSIMETRY		
	ATMOSPHERIC	WET DEPOSITION	DRY DEPOSITION	RESUSPENSION	SURFACE WATER	GROUND WATER	SEDIMENTATION	IRRIGATION	TERRESTRIAL FOODS	AQUATIC FOODS		AIR EXPOSURE	GROUND EXPOSURE	SHORELINE EXPOSURE	WATER EXPOSURE	INHALATION	INGESTION	REFERENCES
STRAP II	A																	Bell & Houghton, 1969
SUBDOSA	A											A						Strenge et al., 1975
TERMOD									A R		A R							Booth et al., 1971 Booth & Kaye, 1971
TRAVIS	A		A	A														Travis, 1975
VADOSCA	R		R		R		R	R	R	R	R	R	R	R	R	R	R	Bramati et al., 1973
WEERIE	A R		A R									A R				A R		Clarke, 1973
WONG																A[b] R	A R	Wong, 1967
WRED	A											A						Cooper, 1969
YIELDS																A	A	Chester, 1974

[a] Include such factors as breathing rate, rate of food intake, occupancy rate, etc.

[b] Includes intake via wounds.

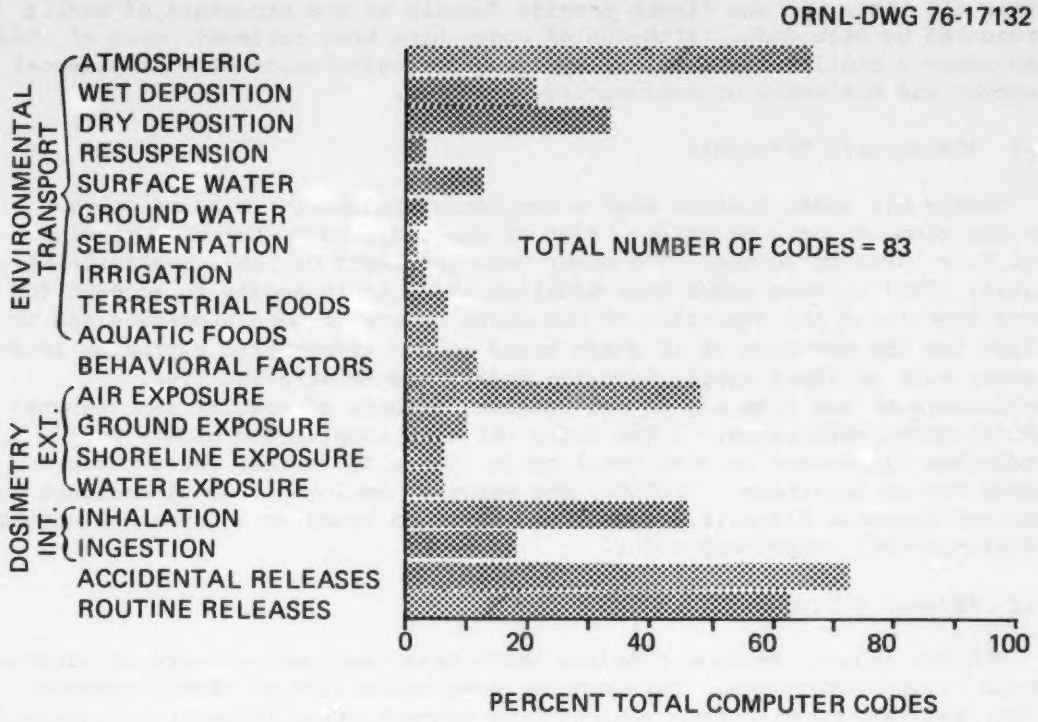


FIGURE 5-2. FREQUENCY OF OCCURRENCE OF VARIOUS FEATURES AMONG EIGHTY-THREE COMPUTER CODES FOR RADIOLOGICAL EXPOSURE (Hoffman et al. 1977a).

Table 5-1 shows that some codes are applicable to a variety of problems whereas others are very specific in purpose and scope. It should be noted that neither the table nor the figure provide details of the structure of models represented by each code. Although 83 codes have been reviewed, many of these codes share a similar mathematical approach for calculation of environmental transport and dosimetry of radionuclide releases.

5.5.2 Atmospheric Transport

Nearly all codes dealing with atmospheric transport are based on the Gaussian plume dispersion model. Most of the older codes use the Gaussian model formulated by Sutton. The newer ones are based on the formulation of Pasquill (1961). Some codes have modified these basic models to account for ground deposition and depletion of the plume by one or more processes and to account for the presence of an upper bound on the atmospheric diffusion layer. However, most of these simple Gaussian models assume straight-line, one-dimensional air flow and do not consider effects of spatial and temporal meteorological variations. A few codes use more complicated models for calculating dispersion on a regional scale (10 to 100 miles) where these effects become important. MESODIF, for example, employs a two-dimensional puff advection Gaussian dispersion model, and ADPIC is based on a three-dimensional particle-in-cell trajectory model.

5.5.3 Aquatic Transport

The few aquatic transport models which have been reviewed are of varying degrees of sophistication. For example, some codes such as ARRRG, CARDOCC, HERMES, and VADOSCA calculate radionuclide concentration in water by assuming a simple algebraic relationship between effluent discharge concentration, a mixing factor, and average turnover rate of receiving water at the point of interest. More sophisticated treatments are represented by codes in which the models are based on the solution to a transport equation. Solution of a one-dimensional transport equation for radionuclides introduced into aquatic systems is computed by the code, TRNSPRT, and a code developed by Armstrong and Gloyna (1968). Two-dimensional transport equations are solved by the finite-element Galerkin model used in GETRA and the finite-difference model used in SERATRA. These codes have been specifically developed for estimating aquatic transport of radionuclides and sediments. ADPIC, DPRWGW, and DPWRCR are in the three-dimensional category. The "particle-in-cell" approach utilized in ADPIC was initially developed for atmospheric transport problems, but the code can, with some limitations, also be adapted to surface water transport. The DPRW codes incorporate generalized transport models using the "discrete-parcel-random-walk" approach.

5.5.4 Food-Chain Transfer

The few codes developed for estimation of transfer and accumulation in terrestrial and aquatic food chains employ a systems approach in which empirically derived transfer coefficients are applied to calculate radionuclide concentrations along various pathways. Transfer from water to aquatic foods is generally calculated through use of a single empirical transfer coefficient called a "bioaccumulation factor," whereas calculation of transfer from air to terrestrial food employs a multiple series of transfer coefficients to account for such phenomena as deposition, vegetation retention, animal grazing habits, etc. Most of these codes have been specifically intended for assessment of routine releases in that the models assume steady-state or equilibrium conditions. The models incorporated in AQUAMOD and TERMOD, however, are time-dependent and can be used potentially for both accidental and routine releases. Unlike other codes, AQUAMOD includes more detail in the description of radionuclide transfers in the aquatic ecosystem, but much of this detail cannot be used because of insufficient empirical data. It is also of interest to note that of the nine codes which can be used to calculate food chain transfer, four of the codes (FOOD, GRONK, ARRRG, and CARDOCC) have been developed from the initial models incorporated in HERMES.

5.5.5 External Dosimetry

About one-half of the codes included in Table 5-1 permit calculation of doses resulting from external modes of exposure. The primary mode of external exposure considered by these codes is exposure to contaminated air. Only about 10 percent of the codes listed in Table 5-1 are concerned with the external doses received from ground, shoreline, or water contamination. The calculation of air exposure is performed assuming a spatial distribution of radionuclides determined by an infinite or semi-infinite uniform cloud model or a finite Gaussian plume model (Slade 1968). The semi-infinite or infinite cloud model is assumed without exception for the calculations of exposure to beta radiation, but nearly half of the codes employ the finite cloud model for calculation of the exposure to gamma radiation. The finite cloud model is used because the semi-infinite and infinite cloud models tend to underestimate the dose received from gamma radiation at distances close to the point of release from elevated sources. Regardless of the type of radiation considered, the codes which calculate external dose from exposure to contaminated water assume an infinite or semi-infinite medium having a uniform distribution of radionuclides. Codes which calculate ground and/or shoreline exposure usually represent ground and shoreline as infinite planes of negligible thickness having a uniform distribution of radionuclides (Hine and Brownell 1956). Only VADOSCA assumes a finite thickness for shoreline contamination.

Although whole-body dose is calculated by all of the codes which consider external dosimetry, only a few codes such as EXREM III, GRONK and SUBDOSA consider the effect of dose attenuation with depth of tissue penetration by radiation. GRONK, however, is an example of a code which employs dose-conversion factors to calculate external dose after concentrations of radionuclides in an environmental medium have been determined. These factors, which consider the effective absorbed energy, the assumed spatial distribution, and the tissue penetration of radiation emitted from radionuclides, are calculated prior to input into the code.

5.5.6 Internal Dosimetry

Most of the models used for calculation of internal doses are those recommended by the International Commission on Radiological Protection (ICRP 1959). Some codes provide only a listing of values for a single parameter which converts intake rate of a radionuclide into dose. These dose conversion factors must be calculated prior to input. Other codes include the detailed parameters of the ICRP models, such as mass of the organ and fractional uptake, retention and effective absorbed energy of the radionuclides. INREM is the only code for which calculation of age-dependent internal doses is stated as a specific objective. The internal dosimetry models of ICRP Publications 10 (ICRP 1968) and 10 A (ICRP 1971) have been incorporated into INDOS I, II, III, and CEDRIC. The ICRP Task Group Lung Model (ICRP 1966) represents the highest degree of sophistication for calculating doses resulting from inhalation of radionuclides. The only codes which have attempted to implement this model to date are AERIN and DACRIN. Neither of these codes, however, considers the additional contribution to total dose resulting from the complete production of daughter nuclides in nuclide decay schemes, except insofar as this contribution has been factored into effective absorbed energy parameters, which are supplied as input.

5.6 AVAILABLE MODELS FOR EXPOSURE TO CHEMICAL POLLUTANTS

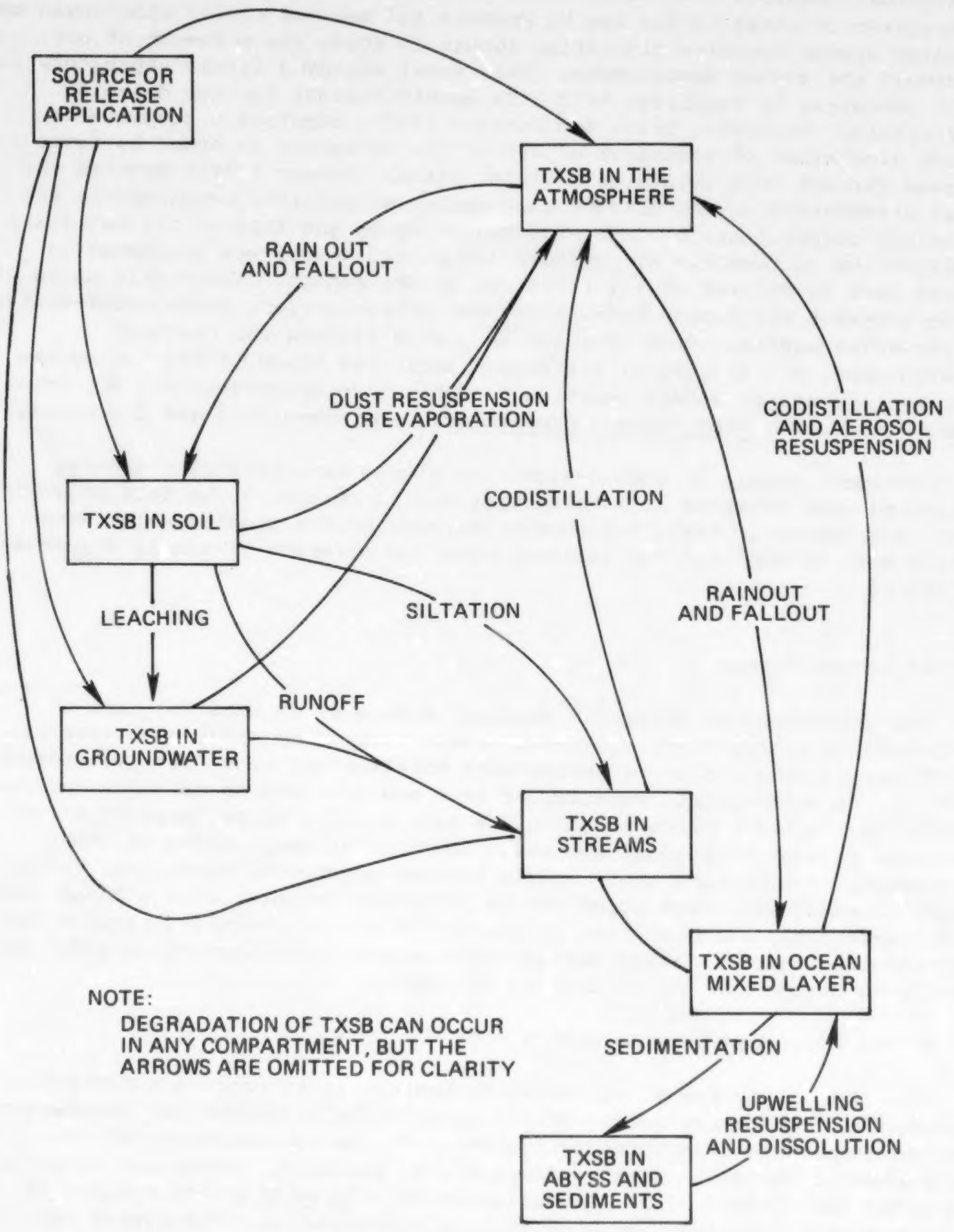
The development of models of exposure for chemical pollutants has been more recent and less concerted than that for radionuclides. The literature on the assessment of models for chemicals in the environment is sketchy and fragmentary. A number of bibliographies is available (Cophenhaver 1974a through 1976b; Corrill et al. 1974; Cophenhaver and Wilkinson 1974a, 1974b; Lehmann 1977, 1978a, 1978b; U. S. Environmental Protection Agency 1977; Cavagnaro 1978a, 1978b; Harnden 1977; Ross 1967).

Most of the models are still in the developmental state and have not been systematically evaluated against concentration measurements in laboratory or field experiments. The available models are generally oriented toward either a particular substance or a particular transport medium. The chemical reactions considered are most frequently lumped into an effective first order decay process that may be valid over a limited range of environmental parameters.

The most frequent formulations focus on the dispersion of a pollutant, usually in a single medium, and in a well defined portion of the environment. Few attempts have been made to formulate the general transport/dispersion processes for the total environment. A general model applicable for relatively stable materials involved over large regions of the environment is sketched in Figure 5-3. Even this relatively complex model omits some potentially important reservoirs such as lakes, lake sediments, and dumps.

Comprehensive models generally emphasize a single compartment such as the atmosphere, the hydrosphere or the lithosphere; however, they treat combinations of these in a very approximate manner. A few global models have been elaborated to describe a multiplicity of compartments for chemical propagation on a large space scale over long periods of time. Separate models for the trophic transfers of the chemical substance throughout food chains may be coupled to the comprehensive environmental fate models as illustrated in a later subsection for aquatic ecosystems.

Several "hybrid" comprehensive fate models have combined interactions in


SOURCE OR RELEASE APPLICATION
TXSB IN THE ATMOSPHERE
RAIN OUT AND FALLOUT
DUST RESUSPENSION OR EVAPORATION
CODISTILLATION AND AEROSOL RESUSPENSION
CODISTILLATION
TXSB IN SOIL
LEACHING
SILTATION
RAINOUT AND FALLOUT
RUNOFF
TXSB IN GROUNDWATER
TXSB IN STREAMS
TXSB IN OCEAN MIXED LAYER
SEDIMENTATION
UPWELLING RESUSPENSION AND DISSOLUTION
TXSB IN ABYSS AND SEDIMENTS

NOTE:
DEGRADATION OF TXSB CAN OCCUR IN ANY COMPARTMENT, BUT THE ARROWS ARE OMITTED FOR CLARITY

FIGURE 5-3. PATHWAYS FOR TOXIC SUBSTANCES (TXSB) IN THE PHYSICOCHEMICAL ENVIRONMENT SYSTEM (from Eschenroeder et al. 1978).

the physical/chemical environment with those in the biotic compartments. Among the earliest of these is the one by Randers and Meadows (1971) which used the Forrester system dynamics simulation format to study the movement of DDT throughout the global environment. This model employed linear representations of all processes by requiring half-life specifications for the dynamics coefficients. Woodwell, Craig and Johnson (1971) reported a compartment systems simulation of transport of DDT in the biosphere in order to trace its progress through food chains on a global scale. Cramer (1972) modeled the global circulation of DDT using a combination of physical compartments and biological compartments to determine the exposure and fate of the material. A comprehensive unification of physical and biotic models was presented in generic form by Gillett et al. (1974) in an EPA report. Three main units of the environment are considered: atmospheric/terrestrial, fresh water-aquatic and estuarine marine. Each of these main subdivisions was further compartmented into structural elements. Haque and Freed (1974) survey the data requirements of models relative to laboratory measurements. The input parameters, termed chemodynamic properties, were identified and discussed.

Transport models in combination with simple mass balancing or mass accounting have provided an interim approach to assessing the fate of chemicals in the environment. Table 5-2 summarizes some of the studies which have applied such an approach for rationalizing the movement of widely dispersed pollutants.

5.7 MICROCOSM MODELS

The philosophy of designing physical models which take the form of microcosms is to reproduce on a small scale various combined processes of biological systems and their environment (Gillett and Witt 1979). Microcosms, which may be terrestrial, aquatic, or both are intended to serve as surrogates for the real world by incorporating the main aspects of pathways of toxic chemicals through biological systems. conflicting goals arise in the development of miniature scale models because regulatory needs call for a single standard microcosm which can be subjected to tests with a large number of different chemicals, whereas laboratory research priorities require the evaluation of many different design concepts and model systems in order to develop an acceptable set of testing systems.

5.7.1 The Microcosm as a Screening Tool

The main objective of microcosm technology is to produce a controlled, reproducible laboratory system that simulates the processes and interactions between components of natural ecosystems. In the laboratory model the environmental variables such as temperature, humidity, light, and water balance are under the control of the investigator as well as the time phasing of introduction of various biotic or nonbiotic components. The system has boundaries containing the components and in general is not self sustaining for long periods of time. The terrestrial systems considered in Gillet and Witt (1979) are described in summary form in Table 5-3. The references cited there give detailed descriptions of the microcosm experiments; therefore, details are not repeated here.

TABLE 5-2 MULTIMEDIA MODELS: REFERENCES AND CHARACTERISTICS

DDT and metabolites	Harrison, H.L., O.L. Loucks, J.W. Mitchell, D.F. Parkhurst, C.R. Tracy, D.G. Watts and V.J. Yannacone, Jr. Systems Studies of DDT Transport. Science, 170:503, 1970. (Mass accounting, mass balance, regional, dynamic).
	Woodwell, G.M., P.P. Craig and H.H. Johnson. DDT in the Biosphere: Where Does It Go? Science, 174:1101, 1. (Mass accounting, mass balance, global, dynamic).
	Randers, J. DDT Movement in the Global Environment. *In*: Toward Global Equilibrium: Collected Papers. D.L. Meadows and D.H. Meadows. Wright-Allen Press, Inc., Cambridge, Massachusetts, 1972. (Mass accounting, mass balance, global, dynamic).
Cadmium	Rupp, E.M., D.C. Parzyck, P.J. Walsh, R.S. Brook, R.J. Raridon and B.L. Whitfield. Composite Hazard Index for Assessing Limiting Exposures to Environmental Pollutants: Application Through a Case Study. Environmental Science and Technology, 12: 802, 1978. (Mass accounting, single source, site specific, static).
Mercury	National Academy of Sciences. An Assessment of Mercury in the Environment. Washington, D.C., 1978. (Mass accounting and mass balance, static, global).
Nitrates	National Academy of Sciences. Nitrates: An Environmental Assessment. Washington, D.C., 1978. (Mass accounting and mass balance, static, not predicting changes, multiscale, local, regional, national and global).
Nitrogen, Phosphorus, and Sulfur	Scientific Committee on Problems of the Environment. Biogeochemical Cycling of Nitrogen Phosphorus and Sulfur. SCOPE 7. Swedish National Science Research Centre, Stockholm, Sweden, 1976. (Global, mass accounting and mass balance, not dynamic).

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TABLE 5-2 (Continued)

Freon and Carbon Tetrachloride	Neely, W.B. Material Balance Analysis of Trichlorofluoromethane and Carbon Tetrachloride in the Atmosphere. Science of the Total Environment, 8: 267, 1977. (Three compartment, global, dynamic, mass accounting).
Chloroform and Carbon Tetrachloride	National Academy of Sciences. Non-fluorinated Halomethanes in the Environment. Washington, D.C., 1978. (Multimedia source inventory and an exposure inventory, no mathematical model, global mass balance).
PCB's	Nisbet, I.C.T. and A.F. Sarofim. Rates and Routes of Transport of PCB's in the Environment. Environmental Health Prespectives, 1:21, 1972. (Mass accounting, continental mass balance, incomplete data on transfer coefficients).
PCB's	National Academy of Sciences. Polychlorinated Biphenyls. Washington, D.C., 1979. (Continental mass accounting, mass balance, not dynamic, multiscale, incomplete data on transfer coefficients).

TABLE 5-3. CHIEF CHARACTERISTICS OF TERRESTRIAL MICROCOSMS USED TO STUDY FATE AND EFFECTS OF CHEMICALS IN THE ENVIRONMENT AS SUMMARIZED IN GILLETT AND WITT (1979).

	Systems					
Characteristic	Plant/soil[1]	Terrestrial monoculture system[2,3]	Microagro-ecosystem[4,5]	Terrestrial Microcosm Chamber[6,7]	Soil care[8,9]	Soil/litter ecosystem respirometer[10,11,12]
Unit size	1.0 liter	19 l.	863 l. (1.5 x 0.5 x 1.15m)	458 l. (1.0 x 0.75 x 0.6m)	40 cc	500 cc
Mass of soil (kg)	0.7	0.4 (vermiculite) 3.0 (Drummer)	165	150	80g	100g
Type of soil(s)	Silty loam; sandy; quartz sand	vermiculite; silty clay loam	Sandy loam	Synthetic potting mix; silty clay loam	Various forest and grassland types	(Douglas fir red alder litter)
Temperature (C)	28/30	26/19	Ambient*	30/19	26/20	19
Light/dark (hrs)	12/12	12/12	Ambient	16/8	12/12	0/24
Air flow rate (l./min)	Ambient	Ambient	2500	10, 50	Ambient	O_2 by demand
Water inputs	Addition to weight; percolation	Addition to weight; post-terrestrial aquatic study	"Rain" to set humidity or excess for percolation	"Rain" to set humidity; "spring"	Fixed volume on weekly basis for percolation	None
Plants	Corn	Corn; soybeans	Corn; cotton; tomatoes; tobacco; cereals and grasses	Alfalfa/ryegrass; Douglas fir/red alder/ryegrass	Endemic plant types (e. g., fescue meadow plants)	None
Invertebrates added	None	Caterpillar slugs, pillbugs, earthworms	None	Tenebrio larvae, snails, pillbugs, earthworms, crickets, Collembola spp., nematode spp.	None (endemic fauna)	None (endemic fauna)
Vertebrates	None	Prairie vole	None	Gray-tailed vole	None	None

(Continued)

TABLE 5-3. (Continued)

	Systems					
Characteristic	Plant/soil[1]	Terrestrial monoculture system[2,3]	Microagro-ecosystem[4,5]	Terrestrial Microcosm Chamber[6,7]	Soil care[8,9]	Soil/litter ecosystem respirometer[10,11,12]
Microbiota	Ambient	Ambient	Ambient	Ambient	Ambient	Ambient
Operating time (per experiment)	Up to 200 days	30 days as terrestrial; 27 days as aquatic	60-90 days	60-90 days	6-9 weeks (including pre-equilibration time of 5-7 weeks)	80 days (including pre-treatment equilibration of about 30 days)

*Greenhouse with supplemental lighting available.

[1] Lichtenstein et al. (1974).

[2] Cole et al. (1976).

[3] Cole and Metcalf (1979).

[4] Beall et al. (1976).

[5] Nash et al. (1977).

[6] Gillett and Gile (1976).

[7] Gile and Gillett (1979).

[8] Draggan (1976).

[9] Ausmus et al. (1979).

[10] Bond et al. (1975).

[11] Lighthart et al. (1977).

[12] Lighthart et al. (1979).

Microcosms permit investigation of interactions that combine physical properties of substances with biological processes while avoiding the costs and risks of full scale field or population system tests. They give indices of time and space distributions of chemical substances thereby providing broad indications regarding the fate and effects of chemicals in the real world. This bypasses the necessity, in some cases, for committing large scale resources to field studies for many chemicals that may be considered. Microcosm experiments, in ideal circumstances, provide a bridge between the laboratory tests of physical and chemical quantities and the expectations for behavior in the external environment. Furthermore, they provide a complex of system interactions in the laboratory that cannot be captured with laboratory bench experiments and may not be under sufficient control for full scale field studies to identify cause-and-effect relationships. Microcosm technology lends insights into interactions and potential effects of classes of chemicals within a controlled laboratory setting. Therefore, it has the potential of providing useful information for guiding the practical aspects of manufacturing, handling and use of chemicals in applications. This provides an advantage over elementary laboratory tests that may provide only limited information for anticipating adverse effects in the field.

5.7.2 Relating Environmental Behavior To Microcosm Data

Since microcosms are not self-sustaining they are not capable of demonstrating some significant ecological processes, such as succession or multigeneration phenomena. It still remains to make inferences from laboratory studies on the components or the processes in order to infer what happens in the open environment with respect to these effects. The number of physical and chemical properties are more directly measurable through laboratory bench tests than through complex systems as represented by those in laboratory microcosms. Physicochemical models are available to extend these fundamental measurements to concentration distribution in the environment as described in the previous section. Physical limitations or logistical limitations may result in an inability to raise or maintain certain environmental interactions of chemical contaminants. These limitations and the questions arising about direct scale-up impose serious requirements on design of the microcosm experiment in view of the assumptions underlying the systems objectives.

In the previous section it was illustrated by example that large differences prevail among the masses of abiotic material and biomass that can be a site for a chemical contaminant. For a given throughput of the chemical substance, therefore, the concentrations can vary widely according to physical and biological processes. The controlling features of the distribution of material suggest scaling rules for the design of laboratory microcosm experiments in order to maintain the correct order of magnitude for various controlling parameters. For example, the ratio of biomass to the mass of water in the system must be carefully selected in order to represent the amount of dilution that occurs and, at the same time, model correctly the exposure of the various organisms to the chemical. Consequently, if an experimental scheme results in one particular organism dominating the available supply of space or nutrients, other effects in the system may be eclipsed by this imbalance. As in any scale model experiments, parameters must be derived and preserved in order to replicate these same physical biological phenomena.

The presence of walls also poses problems with regard to removal of experimental artifacts. Some chemicals may have a greater affinity to the wall surface than to any other element of the system. This creates a situation which may not be representative of phenomena in the open environment. Systematic experiments to test this limitation may be conducted by preserving the ratios of the masses described above and varying the scale of the experiment so that the ratio of certain exposures to the wall surface varies over a wide range of values. In this way the extrapolation to zero wall effect may be possible so that this artifact can be effectively controlled or corrected. If microcosm data are to be used directly to infer behavior of a chemical substance in the environment, generalized similitude rules must be derived in the same manner as that employed for many other scale model experiments. In addition to this derivation the general steps of experimental design must be taken in order to determine how many runs are needed in order to insure accuracy within some predetermined statistical level of certainty.

5.8 A COMBINED MATHEMATICAL/MICROCOSM APPROACH

At the workshop on terrestial microcosms (Gillett and Witt 1979), mathematical and physical modeling were perceived to have an integral relationship directed toward two objectives: 1) a pathway to microcosm development, and 2) a means of providing methodology for testing chemicals in the environment. The coordinated development of mathematical models and microcosms was considered to be an evolutionary process, first concentrating on scientific issues and finally providing a logical framework that would enable the estimation of fate and effects of chemicals on health and the environment. This operational philosophy anticipates the scaling problems of microcosms referred to above and suggests that mathematical modeling can serve to bridge the gaps left by deficiencies in direct scaling.

5.9 EXPOSURE ASSESSMENT

5.9.1 Definition of Exposure

For this chapter *exposure* is defined as the quantity of a substance which reaches the external surface of an organism per unit time, or the concentration of the substance in one or more ambient media. The exposure of an organism may fluctuate in time, and exposure of different organisms in a population may differ. A good exposure model should be able to predict (or explain) not only the average exposure of a group of organisms, but also the statistical distribution of exposure within the group and the temporal fluctuations.

Note that *exposure* as defined above is not synonymous with *intake* or with *dose*. If an organism is exposed by only one route, exposure is related to intake through an intake factor or absorption factor; intake is related to dose through pharmacokinetic and metabolic factors. If an organism is exposed by more than one route, measurement of total intake or total dose may be difficult or complex. For further discussion see the chapter on Biota.

5.9.2 Types of Exposure Models

The function of an exposure model is to relate the exposure of humans or other target organisms to the distribution of a toxic chemical in the environment and ultimately to its sources. Some models are purely predictive: given the distribution and strength of sources and the physical and chemical properties of the substance, the task is to predict the exposure of a target population. Other models are purely explanatory: given measurements of exposure, the task is to trace them back to their sources and to determine the critical pathways which provide the most effective means of control. Most models have features of both types: given some information on both sources and exposure, the task is to relate them in a plausible and self-consistent fashion. If it proves difficult to do so, this often suggests that either the inventory of known source or the measurements of exposure are incomplete.

The primary purpose of exposure assessment is to determine whether or not the exposures constitute a hazard to the target organisms. For this reason, there is no fixed boundary between exposure assessment and health or ecological risk assessment. The nature of the exposure assessment will depend upon the goals of the particular study. For example, if the goal of the study is to ascertain compliance with standards, it may suffice to estimate the maximum level to which an individual might be exposed. The assumption is that if the hypothetical maximally exposed individual is protected, all others will be protected.

In epidemiological studies, an attempt is made to correlate measured exposure levels with observed biological effects, either within or between populations. For this purpose it is essential to estimate exposures of populations and to establish gradients in exposure.

The other major type of exposure assessment study is that designed to investigate whether a chemical may occur at a level suspected to be hazardous. In such studies, the measured or predicted exposure levels are compared with those known to have biological effects, usually on the basis of prior experimentation. Such comparison is usually relatively simple if the environmental and experimental exposures are by the same routes. For example, most aquatic toxicology studies involve exposure of fish or invertebrates to toxicants dissolved in the ambient water at measured concentrations. When an exposure model leads to an estimate of the concentration of the chemical in ambient water, this estimate can then be compared directly with those known to have adverse effects. On the other hand, if the toxicological studies have been conducted by exposing fish to the toxicant in their food, it will be difficult to interpret the potential hazard posed by an ambient concentration unless the relationship between intake via the fills and via the food can be established.

There are sometimes other factors which complicate the assessment of potential hazards posed by exposure. For example, a toxic agent may exist in the environment in a different physical or chemical form from that in which its toxicity was measured experimentally. For example, the toxicity of cadmium in natural organic complexes may differ markedly from that of soluble cadium salts. Also, it may be difficult to assess the potential consequences of fluctuating exposures in the environment if toxicity tests have been conducted only at constant rates of exposure (as in cases where the consequences of intermittant exposure of fish to a chemical in an industrial effluent are to be predicted from measurement of toxicity under continuous flow conditions).

5.10.0 MULTIMEDIA EXPOSURES

The most difficult problems of assessment arise when target organisms are exposed simultaneously by several routes. For example, humans are exposed to carbon tetrachloride and chloroform not only in drinking water, but also in air and food (National Academy of Sciences 1978). Table 5-4 shows estimates of total intake of carbon tetrachloride and chloroform by these three routes: these estimates were derived by combining measurements of exposure with rates of intake (rates of ingestion of water and food, rate of inhalation of air). Estimates of intake by each of the three routes were very variable because of wide geographical variations in exposure, variations in rates of intake, and uncertainty about the efficiency of absorption through the lungs. This illustrates the critical importance of making multimedia assessments of exposure. In this case it is probably reasonable to sum the intakes by all routes to obtain a measure of potential hazard because after absorption these chemicals are distributed through the body and the target organs are distant from the points of entry. However, in cases where toxicological information is available for only one route of exposure and environmental exposure leads to exposure of a different organ (e.g. asbestos ingested in drinking water) it may be difficult or impossible to make a reliable assessment of hazard.

In cases of this kind it may be important to calculate the "dose" to which each tissue is exposed, and this in general requires a pharmacokinetic model of the relationship between the exposure of the organism and the dose to the tissue. The intake of a chemical by an organism depends on the level of exposure, on the physiological properties of the organs via which it is exposed, and on the chemical and physical properties of the chemical. The tissue-specific dose depends on all the above properties and on in vivo metabolism, transport, storage, and elimination. The practical importance of these considerations is that dose limits may sometimes be specified in terms of maximum permissible tissue concentrations. In such cases the exposure assessment must provide comparable data or expected tissue levels.

The necessity for a multimedia approach, even if releases are primarily into one medium, has been demonstrated repeatedly for radioactive materials and is illustrated by application to cadium release from a smelter complex (Rupp et al. 1978). Information on biological effects was related to kidney concentrations of cadmium. The magnitude of an air concentration that would prevent accumulation of a toxic concentration of cadmium in kidneys depended strongly on the fraction of food that was grown and consumed locally. The range of varation was about two orders of magnitude.

TABLE 5-4 (Adapted from NAS 1978)

ESTIMATED INTAKE OF CHLOROFORM AND CARBON TETRACHLORIDE FROM ENVIRONMENTAL SOURCES (mg/year)

Source	$CHCl_3$			CCl_4		
	Exposure Levels			Exposure Levels		
	Min.[1]	Typical[2]	Max.[3]	Min.[1]	Typical[2]	Max.[3]
Fluid Intake	0.04	14.9	494	0.73	1.78	4.0
Atmosphere	0.41	5.2	474	3.60	4.80	618
Food Supply	0.21	2.2	16	0.21	1.12	7.3
Total	0.66	22.3	984	4.54	7.70	629

[1] Minimum exposure, minimum intake for fluids and foods; minimum exposure, 40 percent absorption for atmosphere.

[2] Typical value for exposure and absorption.

[3] Maximum exposure, maximum intake for fluids and food; maximum exposure, 77 percent absorption for atmosphere.

In other cases, measurements and tissue concentrations in exposed organisms may be the only data available for validation of a model. In these cases it is necessary to "calibrate" the system by measuring the relationship between exposure and tissue burden under representative conditions. One example is that of PCB's, for which direct measurements of exposure to aquatic organisms are scanty because of the difficulty of measuring concentrations in water at parts per trillion levels. In this case, measurements of tissue concentrations in fish have been useful in defining geographical patterns of concentration and in relating them to sources (Nisbet and Sarofim 1972; U. S. Environmental Protection Agency 1976). In another example, measurements of concentrations of chlordane components and metabolites in human tissues were used to estimate total exposure by all routes leading to the identification of previously unrecognized sources of exposure (Nisbet 1977).

5.11.0 APPLICATION OF MODELS FROM ENVIRONMENTAL EXPOSURE

In any scheme for hazard assessment of a chemical, biological testing of the target or receptor organism needs to proceed in parallel with the estimation of the expected environmental exposure that will result from the manufacture and use of a new or existing chemical. This section will be limited to the discussion of procedures for exposure assessment but the need for the parallel effort on effects testing should not be overlooked.

No single model can be selected as the best possible for all purposes. The choice of an appropriate model for exposure assessment will depend on the nature of the chemical, the environmental system, receptor of interest, validation potential, cost, and the objectives for which a model will be used. Traditionally models have been selected to predict exposure to an existing pollutant for which monitoring data were available and the adverse effects of which had been identified. The compartment of the environment on which to focus, the spatial and temporal scales of interest, and the critical pathways have been generally known at the start of the modeling effort. The case studies on existing pollutants proved a useful guide for the development of models for classes of compounds with similar physicochemical or chemodynamic properties. The challenge is to provide a systematic methodology for predicting exposure levels that will complement and in time possibly replace the combination of scientific judgement and monitoring information presently used to evaluate environmental hazards. The approach needs to be interdisciplinary, including models for the different compartments of the environment and for transfer across their interfaces.

It is recognized that great uncertainty is associated with the predictions of environmental transport models. Field validation of environmental models for the major classes of chemicals is needed before models are used in making decisions on the safe use of chemicals in the environment. At present, the uncertainty in the transport parameters is such that there is no assurance that increases in model complexity will yield improvement in estimates of exposure. Nevertheless, to the extent that the more complex models simulate the processes occurring in nature more closely, it is expected that these will eventually prove to be the more predictive models. The discussion below of a hierarchical structure for model application is based on the assumption that ongoing and proposed research on model refinement and validation will reduce the major sources of uncertainty in model predictions.

In order to eliminate the unnecessary generation of physicochemical and biological test data on all chemicals, a hierarchy of tests is proposed as shown schematically in Figure 5-4.

At the first level of testing, a simple partioning profile based on the physicochemical properties (i.e., vapor pressure, water solubility, and molecular weight) should be made to estimate whether a chemical will be preferentially located in the air, water, or sediment compartments. The analysis would involve an equilibrium calculation of distribution between the three media, neglecting all degradation or transformation reactions, in order to identify the medium of probable interest.

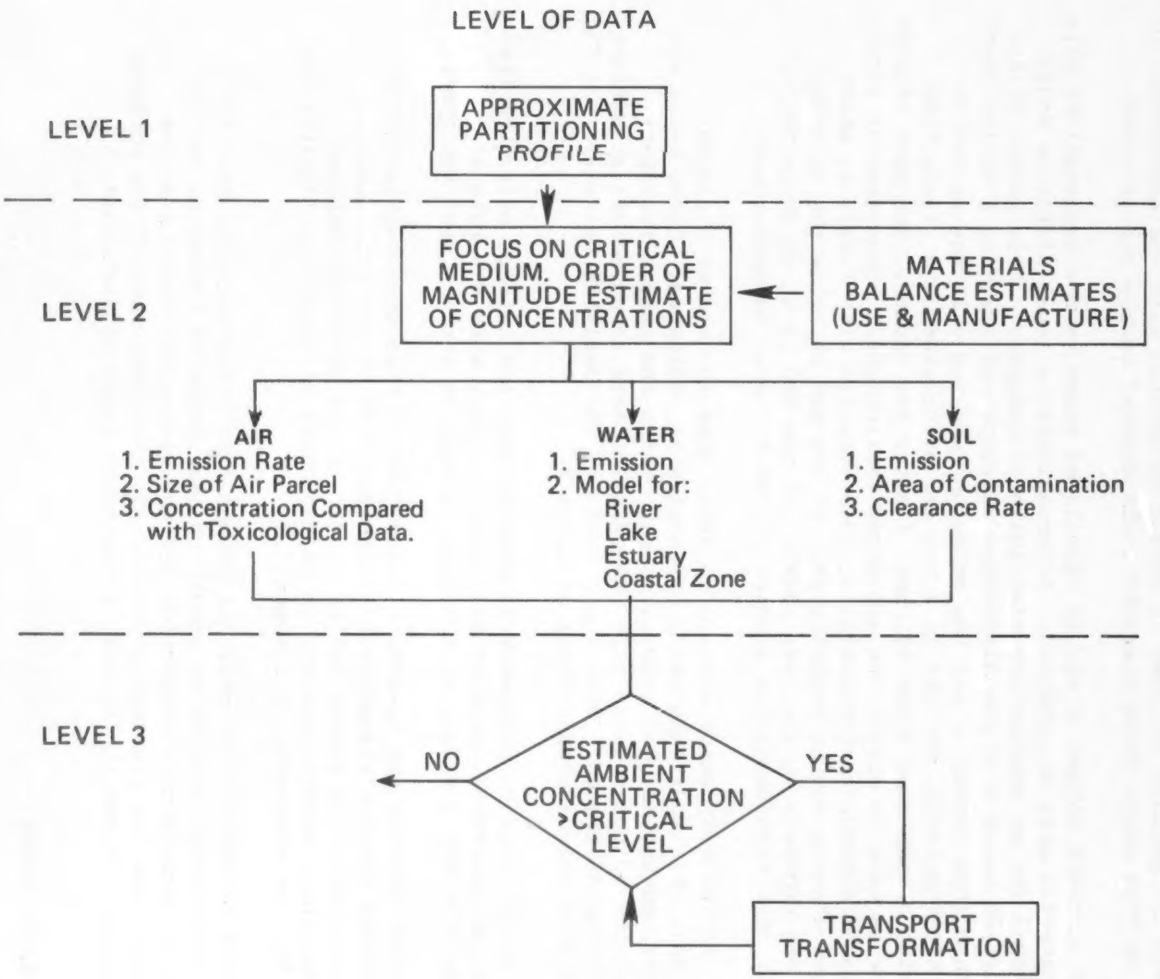
LEVEL OF DATA
LEVEL 1
APPROXIMATE PARTITIONING PROFILE
LEVEL 2
FOCUS ON CRITICAL MEDIUM. ORDER OF MAGNITUDE ESTIMATE OF CONCENTRATIONS
MATERIALS BALANCE ESTIMATES (USE & MANUFACTURE)
AIR
1. Emission Rate
2. Size of Air Parcel
3. Concentration Compared with Toxicological Data.
WATER
1. Emission
2. Model for: River Lake Estuary Coastal Zone
SOIL
1. Emission
2. Area of Contamination
3. Clearance Rate
LEVEL 3
ESTIMATED AMBIENT CONCENTRATION >CRITICAL LEVEL
NO
YES
TRANSPORT TRANSFORMATION

FIGURE 5-4. HIERARCHY OF MODEL DEVELOPMENT. COMPARISON OF ESTIMATED ENVIRONMENTAL CONCENTRATION (EEC) WITH BIOLOGICAL TEST DATA (EFFECTS CONCENTRATION, CR.).

The second level of testing addresses more specific questions of concentration in the compartments of main concern. For this level preliminary estimations of a materials balance are required. This will include estimation of how the material will be used and how it will be manufactured in addition to a preliminary estimation of proposed growth patterns.

Once the use pattern is known it should be matched with the environment of interest. At this stage three standard environmental models are proposed.

1. Air. A standard volume of air is calculated based on the geographical site where the material will be produced. Alternatively, a local diffusion model can be employed for an appropriate time scale of interest. This parcel of air may be described using a simple dispersion equation and assuming a mixing depth of 1 km. Into this parcel of air the emission rate for a 30 day period is inserted. Alternatively, the air in a box can be treated on a steady flow basis assuming a mean wind speed of, say, 1 meter per second. The mass balance on this flow is used to obtain the estimated environmental concentration (EEC). This calculated ambient concentration is then compared with levels at which toxicological effects can be anticipated. If the EEC is below the no effect level then one proceeds to the next level. If the EEC is at or above the no effect level then transformation studies in Level 3 must be undertaken.

2. Water. If the main emissions are to water then the use of a simple dispersion model for four main water categories is indicated. These types are rivers, lakes, estuaries, and coastal zones. Using the proper transport parameter of the selected water body the emission rate is added and an ambient concentration is estimated. This again leads to the decision box where the EEC is compared with the no effect level at Level 3.

3. Soil. If the rate of clearance is greater than the rate of emissions then obviously no environmental problem will result. Only when the rate of clearance is slow and the rate of addition is high is there a need for concern.

If the EEC exceeds the no-effect concentration then more sophisticated models involving various transformation schemes must be utilized (Level 3). While it is a relatively simple matter to set up the materials balance equations depicting transformation, it is much more difficult to identify the parameters for the ecosystem of concern.

The above hierarchal structure is proposed to illustrate the need for developing a screening process to permit concentration of resources for the measurement of chemodynamic properties and for biological testing on the chemicals that pose the greatest problems. In the time-frame of the Workshop only the skeletal framework for such a hierarchy could be developed.

5.12.0 RESEARCH NEEDS

Many of the research needs for multimedia exposure models have been described in other chapters of this report dealing with development and validation of compartment models. Additional research requirements specific to multimedia models involve the definition of transport coefficients between media and the development of optimized strategies for use of multimedia models.

Transport terms which may be casually treated or overlooked in single compartment models include (1) the resuspension of particulates from locations of initial deposition, (2) the exchange rate between suspended and settled sediment in water, (3) adsorption on atmospheric particulates, (4) rain-out of particulate and gas phase pollutants, and (5) the clearance of chemicals from soil.

Multimedia exposure levels involve expenditures for computational efforts and input parameters considerably in excess of single compartment models. Clearly, there is need for developing methodologies for determining when single compartment models suffice or when single compartment models can be linked through simple input-output terms. If simple hierarchal strategies such as those described in the previous section are to be developed there is a need to define scales of space and time in a systematic manner. In view of the limited experience with the use of multimedia models, even for radionuclides, much field work remains to be done to determine specific conditions under which multimedia models are suitable and to determine potential errors with their use. For chemical species undergoing little transformation or a simple first order degradation law this effort would benefit from collaboration with the National Laboratories. Problems of chemical transformation not encountered with radionuclides need further attention. Of particular concern are those where laboratory measurements do not simulate field experience, e.g., photolysis of compounds which can be sensitized in the field by other chemicals and microbial degradation.

5.13.0 SUMMARY AND RECOMMENDATIONS

5.13.1 Utility of Models

A. The most extensive use of transport and fate models to date has been transport, distribution, and fate of radionuclides in the environment. These models have been used to predict exposures and doses to target populations. Most of the available models for radionuclides have been concerned with atmospheric transport and with external dosimetry and internal dosimetry via inhalation. Models of aquatic and terrestrial transport have been less fully explored. Comparatively few multimedia models have been described.

B. Development of multimedia models for toxic chemicals in the environment has generally lagged behind that of models for radionuclides. Most models have been concerned with criteria air pollutants, with waterborne pollutants in rivers, or with pesticides. Recently, some multimedia models have been developed for chemicals such as mercury, PCB's, and chloroform.

C. Problems involved in applying available models to chemicals in the environment include the following:

- The large number of potential pollutants, many of which are produced and released in small quantities at a few locations;
- The lack of important information on sources, environmental behavior, and degradation;
- The lack of understanding of factors controlling intermedia transfer;
- Environmental transformations of one chemical into another.

5.13.2 Present Capabilities

A. Estimates of exposure can be made to within an order of magnitude for chemicals which are already in production and on which information on distribution in the environment and on transport properties is available.

B. Models can be expected to yield only the crudest of estimates of exposure for new chemicals. These estimates may still be useful, however, for identifying the major routes of exposure and for preliminary identification of potentially hazardous chemicals.

C. Modeling, monitoring, and scientific judgment based on experience are all necessary in exposure assessment.

5.13.3 Recommendations For Use Of Models

A. The purpose for which a model is to be used should be specified. The complexity and scale of a model should be matched to the importance of the problem and to the availability of data on model input parameters.

B. Models should be used for the following purposes:

(i) Establishment of priorities for further study and for regulatory action;

(ii) Preliminary assessment of risk;

(iii) Identification of critical pathways and of the relative merits of various control options;

(iv) Identification of important gaps in data, and

(v) Design of monitoring programs.

C. A hierarchical system of exposure models should be used to improve efficiency and to reduce costs:

- Simple models should be explored first, and the results from the preliminary models used to guide the selection of models of increasing detail and complexity;
- The gathering of input data should match the needs of the model at the appropriate point in the hierarchy;
- Each stage in the development of a model should guide the collection of new data as input to the next stage.

D. The sequential development of exposure models should be paralleled by sequential development of testing for effects in order to complete the assessment and to maintain balance in the approach.

5.13.4 Research Needs

A. More information is needed on the location, time distribution, and magnitude of releases of chemicals into the environment.

B. More research is needed into intercompartmental transfer mechanisms, which are less well-understood than transfer processes within compartments.

C. Proposed models should be tested in several critical ways:

(i) Models developed for one chemical or class of chemicals should be tested with another;

(ii) Models developed on a small scale (e.g., microcosms), should be tested with data on the distribution of chemicals over a larger scale;

(iii) Models should be tested for their sensitivity to variation in parameters such as degradation rates or intermedia transfer coefficients.

(D) Measurement programs both in the laboratory and in the field should be conducted for the express purpose of model evaluation.

The Exposure Assessment and Modeling Group participants are listed in Table 5-5.

TABLE 5-5. EXPOSURE/MODELING GROUP PARTICIPANTS

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6.0 REGULATORY ASPECTS OF TRANSPORT AND FATE RESEARCH

6.1 INTRODUCTION

Within the past three decades there has been enormous growth in both the number and amount of chemicals used by society. These chemicals are used as pharmaceuticals, food additives, pesticides, and industrial chemicals.

The manufacture and use of these chemicals has provided society with better health and a higher standard of living. However, the proliferation of chemical usage has elicited concern over the long range effect of these materials on man and his environment. A part of this concern is the realization that many of the chemicals have become widespread environmental contaminants.

In the production and use of many chemicals, it is nearly impossible to avoid the escape of at least small amounts of the material to the environment, either by inadvertence or design. A closed system is not employed in most instances of manufacture and use; thus, conditions exist for chemicals to escape through air and water effluents. In other situations, the chemical may intentionally be released into the environment where it may be transported by air or water to sites well removed from the original source. In the process of transport, the substance may have considerable impact on environmental quality, various species of biota, and may involve contact with humans.

The amount of chemical that escapes is a function of not only the quantity produced and used, but also of the manner in which the chemical is handled by man. Prudent practices can reduce the escape of the chemical and reduce its impact on the environment. Similarly, practices followed in manufacture, handling, and use of chemicals can reduce the hazard to man. Since any chemical in sufficient amounts may be hazardous, the objective in developing appropriate practices and strategies in handling chemicals is to minimize the hazard by control of the quantity that may escape into the environment.

Because of the possible hazards in chemical transport, more must be known about the fate of chemicals entering the environment. Over the years, a body of information has been developed demonstrating the relationship of the properties and reactivity of the chemical to fate in the environment. With this information it is possible to utilize appropriate physicochemical parameters to gain some insight on the transport and fate of a given chemical in the environment.

While a significant body of information has been developed regarding chemical transport and transformation, further elucidation of principles in this area is required for rational regulation of manufacture, transportation, use, and disposal of chemicals. Of particular interest are those principles that may indicate the utility of "benchmark measurements" and the value of "bench-mark compounds" as a guide to the fate of new substances. At present, there are a number of physical parameters of a compound that may be measured and an equal number of processes that may be studied to elucidate transport and transformation . These studies, particularly if conducted in the environment, may require years before definitive answers are obtained. In the interest of protecting man and the environment through rational regulation of chemicals while simultaneously allowing society to benefit from their development and use, reliable laboratory tests providing rapid assessment of transport and fate are needed. Such tests would permit the introduction and utilization of new chemical substances in a reasonable period of time and at a reasonable cost. Similarly, the information gained would provide a basis for developing strategies for minimizing environmental pollution and exposure as well as tactics for safe disposal of the material after use.

In order to prevent significant adverse effects on man or the environment and to provide orderly and expeditious introduction and use of economically important chemicals, thorough research should be supported to develop new and improved test protocols to evaluate transport and transformation of chemicals in the environment. This research should develop tests giving the most reliable predictions while avoiding the accumulation of irrelevant data. These protocols should utilize the minimum number of tests that will produce the desired correlation and reliability, and which allows an assessment of transport and transformation. Such information would aid in the rational and effective implementation of laws and regulations.

6.2 LEGAL REQUIREMENTS FOR CHEMICAL TRANSPORT AND FATE DATA AND THEIR USE IN REGULATION

6.2.1 Toxic Substances Control Act (TSCA) PL94-469

TSCA does not explicity require the obtaining of chemical fate information but the law contains several features which implicitly lead to that requirement.

Section 2b of TSCA states that "It is policy...that...adequate data should be developed with respect to the effect of chemical substances and mixtures on health and the environment and that development of such data should be the responsibility of those who manufacture and those who process such chemical substances and mixtures".

In Section 3(5) the term environment is defined as including water, air and land, and the interrelationships which exist among and between water, air, land, and all living things.

Section 4 of the Toxic Substances Control Act (TSCA) is principally concerned with existing chemicals which will be listed on an inventory being prepared by EPA. The section states that if the administrator finds that the manufacture, distribution, processing, use or disposal of a chemical substance or mixture may present an unreasonable risk of injury to health or the environment, and that there are insufficient data and experience to reasonably determine or predict such risk, and that testing is necessary to develop such data, or that there is, or may be significant or substantial human exposure, the administrator shall by rule require testing to develop relevant data.

Section 5 of TSCA requires EPA to control new chemicals or significant new uses of existing chemicals but does not grant to EPA authority to require testing of a new chemical. However, EPA is required to assess the risk posed by new chemicals to health or the environment. This risk assessment will be based partly on the requirement that manufacturers submit all relevant test data in their possession or control to EPA which has 90 days to perform this risk assessment (extendable to 180 days). If within that time period EPA makes a determination that the proposed use, manufacturing, processing, distribution, or disposal activities will present an unreasonable risk to health or the environment, EPA can regulate those activities. If EPA finds that there is insufficient data to assess the risks posed by the chemical, and the use, manufacturing, etc., of the chemical may present an unreasonable risk to health or the environment, or there will be substantial exposure to man or the environment, EPA can regulate the chemical until the necessary data are developed.

Because of the difference in wording with respect to existing and new chemicals, the Office of Toxic Substances (OTS) will be formulating rules for testing existing chemicals and presenting guidelines for the testing of new chemicals. The guidelines will provide some counsel to manufacturers of new chemicals regarding EPA's position on the kinds of information necessary to assess the potential for unreasonable risk.

With respect to the information which the Agency would like to have in order to make such an assessment, there should be little difference between existing and new chemicals. One key determination will be the expected or estimated environmental concentration (EEC). One of many elements which determine EEC is the fate of the chemical in the environment(s) under consideration. Fate, in turn, may be viewed as consisting of transport and persistence possibilities. An analysis of potential transport mechanisms leads to the conclusion that certain physical and chemical data should be considered. Depending on the nature of the specific chemical, such data may include solubility in water, the vapor pressure, the octanol/water partition coefficient, pH, density, particle size, and other data as discussed in the proposed Section 5 guideline drafts. Certain data may be used to predict volatility and soil/sediment adsorption possibilities. EPA would like to have information on biodegradation, photolysis, hydrolysis, abiotic oxidation/reduction, and dissociation possibilities in order to predict persistance.

The rules and guidelines will specify the methodology EPA believes appropriate to obtain the kinds of data discussed. These data will be used in making detailed assessments of the potential risks. Although it is believed that such data are essential in assessing risk, fate data and estimates are only part of the many factors which must be considered in the assessment.

Careful consideration of the test plan and the sequencing of tests should reveal relatively few chemicals that will need to undergo the entire set of tests. Factors which will influence the decision on which tests to run will include the known physical and chemical properties of the chemical and the ways in which the substance is or will be manufactured, processed, transported, used, and disposed.

In the course of developing testing guidelines, EPA has considered a number of tiered testing systems which have been proposed by various interested parties and some which have been developed within OTS. Generally, these test schemes tend to contain basic physical and chemical properties and short-term persistence and acute toxicity tests in the "lowest" or "first" tier and longer-term, more costly tests in the higher tiers. The higher tier tests might include the use of radiolabeled test material, the determination of metabolic intermediates, and some sort of mass balance in biodegradation testing. Another example of a higher tier test would be the determination of the "effective vapor pressure" and volatility rate of a chemical mixed in a well-defined soil under controlled soil moisture, air humidity, air flow, and temperature conditions.

The first tier tests are often called "screening tests" and while they provide a predictive first approximation, more elaborate studies conducted in the higher tiers may be required. There is a need to develop satisfactory decision criteria for progressing from one tier to the next. Defining the nature and sensitivity of decision triggers will have a great deal to do with the expense of testing a substance as well as with the desired degree of certainty that the system will yield a low percentage of false negatives and false positives.

6.2.2 Federal Insecticide, Fungicide and Rodenticide Act (FIFRA)

On July 3, 1975 EPA promulgated final registration regulations in 40 CFR Part 162 Subpart A. These regulations established the basic requirements for registration of a pesticide product. Section 162.8(b) (3) (ii) Environmental Chemistry lists the kinds of data the Agency would generally require to register a pesticide intended for "outdoor application", as that term is defined in 40 CFR S162.3(cc). The term includes any pesticide intended for outside application or whose consequences would be used to define what chemical substances remain in the environment after a pesticide is used, how long and at what levels the residues persist in the environment, and where the residues are likely to be found in relation to where the product has been used. The kinds of data required in Section 162.8(b) (3) (ii) to evaluate a pesticides' environmental chemistry characteristics include, but are not limited to: field stability data on the active ingredient(s) indicating the dissipation time and its modes of degradation and/or metabolism; persistence, degradation and accumulation data for target and/or non-target species for the active ingredient(s), metabolite(s), or degradation product(s); and mobility data for the active ingredient(s), metabolite(s) or degradation product(s) including volatility and leaching properties. Environmental chemistry information in support of safe methods for the disposal of the pesticide formulation and pesticide containers is also required under this subsection.

Under the authority of Section 3(c) (2), 8 and 25(a) of FIFRA, as amended, the Agency published proposed Guidelines on June 25, 1975 and again on July 10, 1978 which described with more specificity the kinds of data which must be submitted to satisfy the requirements of the registration regulations. The proposed Guidelines specify the conditions under which each particular data requirement is applicable to a pesticide product, the standards for acceptable testing, stated with as much specificity as the current scientific disciplines can provide, and the information required in a test report. The appendicies to the Guidelines provide useful information and references for designing test protocols and, in some cases, examples of acceptable protocols for conducting the required testing.

Environmental Chemistry data requirements specified in Section 163.62 as proposed Guidelines in the Federal Register, July 10, 1978 greatly expand upon but generally parallel the basic registration requirements outlined in Section 162.8(b) (3) (ii) of the FIFRA Section 3 Regulations for Environmental Chemistry. Section 163.62-12, which is reserved in the current Guidelines, will also contain requirements for environmental chemistry data which would be used with other data to establish safe reentry intervals. Section 163.63-13 will be revised at some future time to establish specific data requirements concerning the disposal and storage of pesticides.

6.2.3 Regulatory Aspects of Transport and Fate of Chemicals in the Environment as Related to Resource Conservation and Recovery Act (RCRA), 1976

The Solid Waste Disposal Act as amended by the Resources Conservation and Recovery Act of 1976 (P.L. 94-580 [October 21, 1976]) provides (1) for improvement of practices in solid waste disposal to protect public health and environmental quality, (2) for control by regulation of hazardous waste from the point of generation to the point of disposal, and (3) establishes resource conservation as the preferred solid waste management approach.

The definition of solid waste (Section 1007 [27]) encompasses garbage, refuse, sludges, and other discarded materials including liquids, semi-solids, and contained gasses (with a few exceptions) from both municipal and industrial sources. Subtitle C of the act creates a "cradle-to-grave" management control system for hazardous waste, a subset of all solid wastes. Solid waste which is excluded from subtitle C will be subject to the requirements of subtitle D of the Act, under which open dumping is prohibited and environmentally acceptable practices are required.

Subtitle C consists of seven sections that establish a hazardous waste program. Section 3001 requires EPA to define criteria and methods for identifying and listing hazardous wastes. Those wastes which are identified or listed as hazardous are then included in the management control system constructed under Section 3002-3006 and 3010.

Section 3002 addresses the standards applicable to waste generators and announces the mechanics of the manifest system to track waste transported from the point of generation to its ultimate disposition. Section 3003 authorizes standards for transporters of hazardous waste, to assure that such waste is carried carefully. The Agency has attempted to coordinate closely with Department of Transportation regulations.

Section 3004 addresses standards affecting owners and operators of hazardous waste treatment, storage, and disposal facilities. These standards define the levels of human health and environmental protection to be achieved by these facilities and provide the criteria against which EPA (or state) officials will measure applications for permits. Facilities on a generator's property as well as off-site facilities are covered by these regulations and do require permits; generators and transporters do not otherwise need permits.

Section 3005 regulations set out the scope and coverage of the actual permit including the granting process for facility owners and operators. Requirements for the permit application as well as for the issuance and revocation process are defined by regulations under 40 CFR Parts 122, 124, and 128. Section 3005(e) provides for interim status during the time period that EPA or the states are reviewing the pending permit applications. Special regulations under 3004 apply to facilities during the interim status period.

Section 3006 requires EPA to issue guidelines under which states may seek both full and interim authorization to carry out the hazardous waste program in lieu of the EPA-administered program. States seeking authorization in accordance with Section 3006 guidelines need to demonstrate that their hazardous waste management regulations are consistent with and equivalent to EPA regulations under sections 3001 -3005.

Section 3010 requires any person generating, transporting, owning, or operating a facility for treatment, storage, and disposal of hazardous waste to notify EPA of this activity within 90 days after promulgation or revision of regulations. The notification should identify and list a hazardous waste subject to Subtitle C regulation and the waste may not be legally transported, treated, stored, or disposed after the 90 day period unless this timely notification has been given to EPA or the authorized state during the above 90 day period. Owners and operators of inactive facilities are not required to notify.

Most of the hazardous waste regulations discussed above have been proposed in the Federal Register and should be final by January 1, 1980. Sections 3001, 3002, and 3004 were proposed on December 18, 1978, Section 3003 on April 28, 1979, Section 3006 on February 1, 1978, and Section 3010 on July 11, 1978. Section 3005 will be proposed and Section 3006 reproposed under authority of the Clean Water Act.

In order to develop and implement regulations, research should be applied to some of the unknowns regarding transport and fate of a variety of hazardous wastes destined for treatment, storage, or disposal on land. Research is needed on the movement of chemical pollutants through all media and especially clay soil, the mechanisms of adsorption and desorption, the release of volatiles from the soil and vapor phase transport, the effects of disposal on the hydraulic conductivity of soil, and techniques for monitoring leachate and groundwater at land disposal sites.

6.2.4 Safe Drinking Water Act of 1974 (PL93-523)

Under this act, the administration is required to regulate any substance that may have an adverse effect on man. Regulation may be accomplished either by setting a standard or by requiring treatment to remove the hazard. Synthetic organic chemical contaminants in drinking water originate from organic chemical contaminants derived from chlorination practices at the water plant (Trihalomethanes or THM's), while organic chemical contaminants in the water source derive from direct or indirect industrial discharges, agricultural sources (pesticides), and runoff.

The proposed regulations address these sources separately. Trihalomethanes are to be controlled by means of establishing a Maximum Contaminant Level (MCL) of 0.10 milligrams per liter (mg/l) (100 micrograms per liter). Synthetic organic chemicals of industrial origin are to be controlled by treating the water in granular activated carbon (GAC) or the equivalent. The time schedule for installation and operation of GAC in affected systems (those that do not receive a variance) is 5 years from promulgation.

With respect to chemical fate (transport and persistence) information, the Safe Drinking Water Act and its administrators focus on the assurance that certain undesirable constituents do not appear in drinking water above defined maximum concentration levels.

6.2.5 Clean Water Act of 1977 (PL95-217)

This act is an amended form of the Federal Water Pollution Control Act, which was last amended in 1972. The objective of the act is "to restore and maintain the chemical, physical, and biological integrity of the Nation's waters." The act covers a multitude of water-quality related subjects, including research, grants for construction of treatment works, standards and enforcement, permits and licenses, and many other general provisions. The act directs EPA's Administrator to "prepare or develop comprehensive programs for preventing, reducing, or eliminating the pollution" of ground and surface waters in the United States. As part of these programs, the Administrator is required to "conduct and promote the coordination and acceleration of research, investigation, experiments, training, demonstrations, surveys, and studies relating to the causes, effects, extent, prevention, reduction, and elimination of pollution."

The terms "transport" and "fate" of chemicals do not appear in the act. Nevertheless, transport and fate information are probably necessary for EPA to fulfill the requirements of several of the sections of the act. These sections are discussed below.

6.2.5.1 Section 307 - Toxic and Pretreatment Effluent Standards

Section 307 (a) (1) requires the Administrator to publish a list of toxic pollutants. He also has the authorization to add or remove pollutants from this list but must "take into account the toxicity of the pollutant, its persistence, degradability, the usual or potential presence of the affected organisms in any waters, the importance of the affected organisms, and the nature and extent of the effect of the toxic pollutant on such organisms." Since transport and fate information is necessary to determine persistence and degradability of the pollutants, this information is necessary whenever the Administrator adds to or removes from the toxics list. Currently the list contains sixty-five compounds, substances, and groups or classes of compounds.

Section 307 (a)(2) provides EPA the opportunity to require effluent limitations on a pollutant-by-pollutant rather than industry-by-industry basis as provided elsewhere in the act (S.301). When requiring these effluent limitations, the Administrator is directed to consider the same things as under Section 307 (a)(1) including persistence and degradability. Therefore, some transport and fate information is needed for effluent limitations under Section 307.

6.2.5.2 Section 304 - Information and Guidelines

Under this section, the Administrator is required to develop and publish water quality criteria which shall reflect the "latest scientific knowledge... on the concentration and dispersal of pollutants, or their by-products, through biological, physical, and chemical processes."

6.2.5.3 Section 403 - Ocean Discharge Criteria

Section 403 (c)(1) requires the Administrator to promulgate guidelines for determination of the degradation of the waters of the territorial seas, the contiguous zone, and the oceans. Among other things, these guidelines are to include "the transfer, concentration, and dispersal of pollutants or their by-products through biological, physical, and chemical processes," and also pollutant persistence.

There are also several other sections of the act where transport and fate information may be useful in determining potentials for water quality deterioration, although the language of the act does not specifically call for it. In Section 311, Oil and Hazardous Substance Liability, transport and fate data are used in support of regulation to control industrial effluents and to identify candidates for the toxic pollutant list under Section 307 (a)(b) of CWA (1977). Transport and fate data are also used in screening candidate chemicals to identify "red flags" used in risk assessments to determine if a candidate meets requirements of the list.

To determine regulatory options for pollutants not controlled by BAT developed under Section 301 of CWA (1977) [Section 307 (a)(2)], transport and fate data are used in the early warning (Action Alert) phase which identifies "red flags", if any, and gives presumptive indicative of risk. The data are also used in risk assessment to get quantitative determination of risk and identify critical pollutant sources which "drive" that risk.

As part of predictive exposure quantification, transport and fate information is used in conjunction with source identification to predict quantities lost to the environment and the environmental compartment to which the chemical is lost. These results are subsequently confirmed by monitoring. Finally, the data are needed in conjunction with monitoring to help identify unsuspected sources when monitoring is the first indicator of potential risk ("red flag"), as part of observed exposure quantification.

Other areas not directly limited to aquatic parameters where transport and fate data are needed include source ranking, identification of other media if regulation beyond CWA must be considered [Section 307 (a)(2)], and completion by multimedia mass or materials balance.

These fate (transport and transformation) data are used in one aspect of the CWA to provide one basis to quantify exposure for specific quantitative risk assessment, and to permit system identification to the most important regulable sources of pollutant subject to that risk assessment. The latter is the more directly regulative of the two basic uses of job data.

6.3 NECESSARY DATA FOR ESTIMATING EXPECTED ENVIRONMENTAL CONCENTRATIONS AND/OR EXPOSURES

6.3.1 Introduction

The subject chemical and the various media of the environment in which the chemical exists are two interacting factors to consider in the transport and transformation of chemicals in the environment. Each medium has its own physical, chemical and biological properties to be considered for interaction with other media. These interactions are facilitated by weather (wind, sun, rainfall, etc.) which transports and disperses or concentrates both the chemical and the media in varying proportions to each other. Concentration of chemicals in the environment are rarely at a steady state for long periods of time so that hazard assessment must be related to changing concentrations and their toxicity to organisms.

6.3.2 Quantity of Chemical

The total quantity of a chemical released to the environment is important in respect to its distribution in areas of different size (National Academy of Sciences 1975b; National Institute of Environmental Health Sciences 1977). The chemical may affect, or be affected differently by, the surrounding media if it saturates or does not saturate the media. Water runoff of a chemical from small areas into streams may be quantitatively different from runoff from large areas. Since some chemicals have many uses, all of the uses and eventual disposition of the chemical, whether alone or in a product, must be accounted for and environmental concentrations predicted for various media. This is particularly true with persistent compounds since even compounds of low volatility can be transported significantly in air or water.

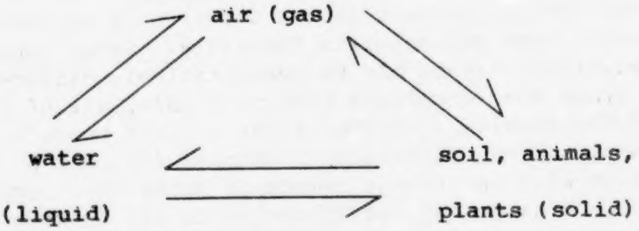
6.3.3 Physical Dilutions of Chemicals Applied and Transported to Various Segments of the Environment

Knowledge of the potential for physical dilution of chemicals in a given receiving medium is important, especially if little or no degradation or transfer occurs in the original medium (Hamaker 1972). Dilutions are significant because of the resulting concentration of chemical and the intensity of the effect produced by it. Because the range, area, weight, volume of soil, water, air, and organisms are difficult to visualize, a summary of data on representative-sized samples of these media on earth are needed to estimate comparative and representative dilution factors. These dilution factors in water are applicable to various ecosystems such as large and small bodies of water which are flowing or still, or land areas of various sized drainage basins with varying climates, soils (or lack of soils) and soil coverage. Important factors are air movement, evaporation rates of chemicals, and the water and particulate content of air and their clearance rates from air due to precipitation.

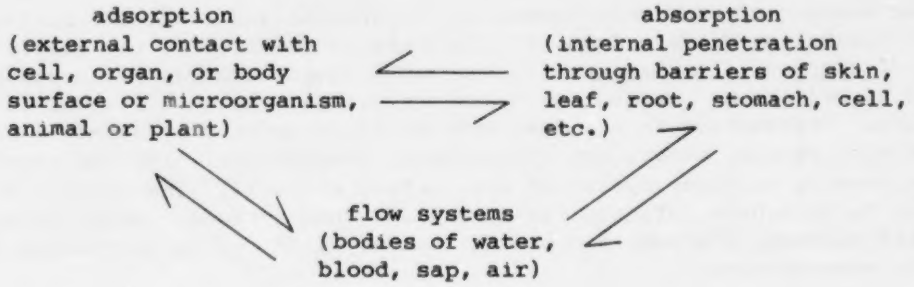
Data on air and water turnover rates for various areas of the United States, for example, include average annual values for water runoff on land of various slopes, elevation, and vegetative coverage, wind speeds, and monthly temperatures. The representative values of these measurements need to be worked into a skeletal chart for ballpark references to be used in calculating and modeling environmental concentrations.

Volatility, condensation, and freezing are changes in water which interrelate with the transport of water soluble compounds. Rainfall, wind movement, and temperature are all important weather factors which help determine transport of chemicals between various media such as air-water, water-air, soil-air, and air-soil, etc. Data on the long distance transport of chemicals by wind or by rivers carrying treated soil particles require knowledge of the range of size, volume, and weight of the particulate load carried by such transportation means.

All chemicals may exist in gas, liquid, and solid phases in various ratios which are temperature-, pressure-, and solubility-dependent. These phases are always striving for a balance in complex biological systems such as pictured below:



Within biological systems, equilibrium is rarely if ever reached since organisms must use energy to replace cells, grow in size or numbers, respire, and excrete. Therefore, organisms demand a constant flow in respiration, nutritional, and excretion systems. Major liquid flow systems in plants and animals are supplied by water externally. Internally, they are supplied by water in the form of blood in animals and sap in plants. Uptake and distribution of chemicals in biological systems, whether within or between organisms and their external environments, involves several phases which can be simplistically pictured as:


adsorption
(external contact with cell, organ, or body surface or microorganism, animal or plant)
absorption
(internal penetration through barriers of skin, leaf, root, stomach, cell, etc.)
flow systems
(bodies of water, blood, sap, air)

The tendency of a compound to adsorb onto a given surface is related to its inherent chemical and physical properties and is reproducible under standardized test conditions (National Academy of Sciences 1975b; National Institute of Environmental Health Sciences 1977). Chromatographic analytical methods are used by chemists in separating and identifying compounds from a mixture of chemicals. Similarly, the separation of sediments and dissolved materials in natural waters is analogous to a giant chromatographic system in the way in which it separates compounds by adsorption on various natural surfaces. The ratios of separation of a given chemical between liquids, solids, and/or gases have been described as partition or distribution coefficients or as adsorption coefficients between solids and liquids or solids and gases. The properties of chemicals which are key indicators for estimating typical distribution coefficients are solubility (especially in water and fat solvents), vapor pressure and the interfacing surface energy forces, whether mutually attractive or repellent (anionic, cationic, pH, polarity, and other electrical forces).

The laws of physics and chemistry can be used to predict volatility, and air-water, water-solid, and air-solid partition relationships under ideal conditions. Under practical conditions, the same compound may volatilize readily from glass, poorly from wood, and decompose on copper surfaces. Thus, while surface layers of molecules may act according to these laws, adsorption and absorption may play a large part in determining what percentage of the dose of a chemical applied to the surface of a solid object is available for exchange to air or water. Once absorbed in a solid, the chemical may be "metered" back out to the surface at a given rate dependent on the interaction of the physical and chemical properties of the chemical and substrate and various transport mechanisms. Aeration rates of water due to water turbulence and wind are important in chemical dilutions.

6.3.4 Degradation

Degradation of chemicals usually occurs at different rates in different media and under different climatic conditions. Half-life determinations or estimations are needed for representative media such as water, soil, animals, plants, and microorganisms (Hamaker 1972).

Degradation of chemicals occurs in the animate and inanimate world. Animate metabolism differs from the inanimate degradation by the catalytic action of enzymes, cellular growth, and rapid fluid turnover rates via blood or sap and by excretion. Metabolism takes many routes, often different in diverse organisms. Degradation in the inanimate world is greatly affected by climatic factors such as air, water, sun (photolysis, temperature), and the physical factors causing turnover cycles of air, water, and soil. The actions of these climatic factors have infinite variations and combinations. Nevertheless, these are minimum, average, and maximum values which can be calculated from standard measurements.

The degradation of chemicals can take place in many ways, depending on the above variables, and reactivity of the subject and the chemical itself, such as hydrolysis, oxidation, dehydrochlorination, dechlorination, alkylation, condensation, ring fusion, ring breakage, pyrolysis, photolysis, etc. Knowledge of the structure and reactivity of a chemical helps to predict the major route(s) of degradation. The fact that degradation routes are often multiple may complicate calculation of half-lives.

6.3.5 Estimation of Concentrations

Estimation of concentrations of a given chemical to be applied to a given environment at a given time must take into account the complicated combinations of use, quantity, dispersion via physical dilution and transportation, partitioning between various environmental segments as related to climate, the natural history of organisms, and the action of man. These factors are all important in the estimation of the fate of chemicals in the environment and expected concentration and time of exposure of organisms to them.

A comparison of laboratory experimental data, theoretical data, and field experimental data must be a continuing exercise to strengthen and substantiate useful correlations, from which to make data predictions and for use in models.

6.3.6 Useful Measurements

The usefulness of physical-chemical properties for assessing the probable transfer and transformation of chemicals in the environment depends on accurate interpretation of the test data.

Table 6-1 presents a list of parameters often found to be of value in assessing transport and fate but it is not intended as a check list of tests equally useful under each law for each chemical. Rather, the table demonstrates the type of information that has been found to be valuable in characterization of the chemical, propensity of the chemical to be transported, and

TABLE 6-1. TYPES OF DATA OF VALUE IN ASSESSING TRANSPORT AND FATE OF CHEMICALS†.

	FIFRA	TSCA	CAA	CWA	RCRA
Elemental Composition	+++	++	+	++	+++
Structure	+++	++	+	++	+++
MP	++++	+	+++	+++	+++
BP		+		+++	
Subl. Point		+			
Vapor Pressure	++++	+++	++++	+++	+++
Sol. H_2O Org. Sol.	++++	++++		+	+++
Kp	++++	++++			
Sp Gr	++++	+			
Ki	++++	++			
pH		+++			
Hydrol	++++	++++	++++	++++	+++
Photol	++++	++++	++++	++++	
Metab Terr. Aquatic	++++	++++		+++	+++
Leaching	++++	+++			++++
Ads./Desorb		+++		++++	++++
Oxdn.	++++	++++			
Field Tests	++++		++	++++	
Residues Fish Crop	++++	++++		++++	
RXN Rate			+++		
Fallout/Rainout/Deposition			++		
Particle Size		+	++++		

†PSAC 1973, NAS-B 1975, NIEHS 1977, ACS 1978, Goring 1972, Hamaker 1972, Freed, Chiou and Haque 1977.

*Potable water regulators concerned with specific ingredients in water and specifying limits (maximum allowable concentrations) in the water. Examples are coliforms, certain metals, certain chlorinated organics, chemical fate has not been a direct concern.

indicate some of its reactions as related to persistence in the environment. The number of +'s indicate the possible utility of the measurement for certain chemicals under given conditions. The relative utility of these properties depends on the circumstances of use and exposure in the various environmental segments in which the fate of the chemical must be determined. When such values have been obtained and ranked in comparison with other chemicals, a reasonable estimate of the routes and rates of transformation and fate may be ascertained.

Estimates of environmental concentrations and fate of chemicals in the environment are important parameters necessary to regulate chemicals in relation to their use and toxicity. Presently, estimates of the transport and partitioning of chemicals in the environment are based on physicochemical parameters. However, estimates of the chemical fate of the substance is more difficult because of our lack of precise information on the interaction of environmental forces and processes bringing about chemical alteration.

Concentrations may be accurately assessed on empirical data such as vapor pressure, water solubility, soil adsorption, coefficients, etc., but more research is required to attain the same level of ability to predict the fate of a chemical under the varied environmental conditions. For example, it is a highly complex problem to attempt to estimate the mass balance of a chemical in water containing sediments or the runoff concentration from soil on which chemicals are heavily or lightly adsorbed. This arises from the multi-step processes of chemical transfer and reactions encountered in a complex system.

6.3.7 The Role of Model Ecosphere in EPA Regulations

The environment is a multiphase system involving air, biota, soil/sediment, and water. It appears cost-effective to develop model systems that take into account the interactions of chemicals within all of these compartments. For example, a volatile chemical may be deposited on land, released to the air, and washed by precipitation into the water where it may accumulate in aquatic organisms; some of the latter may then enter the human food chain, and complete the pathway of the ecosphere. The problems of studying how the various environmental compartments interface should be the subject of intensive research by EPA. There is a recognized need for establishing whether an individual compartment's model can be used as input for all other compartments of the multimedia model or whether all compartments must be modeled as a unit.

The relationship between mathematical models and microcosms is unclear as to whether they are complementary or redundant. Whatever approach is followed requires validation by actual environmental monitoring studies. For modeling to be an effective tool, EPA must make statements regarding the level of precision required for the data output. The modeler, on the other hand, must establish amd make known the effect of the quality of the input data on the ability of his model to achieve the EPA's goals. Research is also needed to delineate and describe the minimum number of critical parameters needed to do an effective modeling exercise. The need for meteorological data should not be ignored. Similarly, cognizance must be taken toward limiting or augmenting processes, factors and responses (i.e., sensitivity analysis).

The use of validated models for analogous compounds, thereby eliminating the need for extensive testing on those compounds, needs to be explored. Criteria for the applicability of these model systems needs to be developed recognizing that a single model probably does not serve all compounds (i.e., organic versus inorganic, low molecular weight organics versus polymers).

Strong cooperation is recommended between program offices of EPA in establishing the most suitable data requirements for developing models to serve their respective program needs keeping in mind the need to strive for uniformity of approach. It must be recognized that the only output that can be expected from any of these models is the expected environmental concentrations (EEC) and that coupling with toxicological data is needed for risk analysis. Simplified models based on a limited number of parameters are needed to quickly screen for problem chemicals. The identification of trigger mechanisms and discipline of criteria to short-circuit the collection of unnecessary data should be an integral part of the research to establish these simplified models or screening systems.

6.4 THE EXTENT TO WHICH THE SAME CHEMICAL FATE PARAMETERS CAN BE USED BY DIFFERENT EPA OFFICES

One of the major goals of the EPA is to prevent chemical pollutants from causing adverse effects on man and the environment (Maugh 1978). Assessing the potential hazard of a compound requires information about toxicity and predicted exposure levels of the substance to non-target organisms. Environmental fate and transport tests currently under development will be used to predict what will happen to a chemical once it enters the environment. These tests will ultimately allow the prediction of exposure levels based on environmental mobility and degradation routes.

The Toxic Substance Control Act (TSCA) and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) address the problem of environmental fate and transport most specifically. Both acts have requirements and suggested procedures for generating environmental fate and transport information. The Clean Air Act (CAA), Clean Water Act (CWA), and Resource Conservation and Recovery Act (RCRA) do not require such data but must be concerned with predicting what might happen to a harmful chemical entering the environment instead of only assessing the consequences after the fact. Therefore, chemical fate and transport parameters should be of universal concern. Although some EPA offices may require more detailed information (more intensive testing) than others, they all share a common goal of accurate estimates of exposure levels from transport and fate data (Culleton 1978).

The different EPA offices should be encouraged to use the same chemical fate and transport parameters wherever possible. An EPA-wide testing scheme may be the most efficient approach for determining these parameters. Basic chemical information may be obtained from initial screening tests. At this initial level, standardized test methodologies should be used to provide a uniform set of information for all compounds. The screening tests should evolve through use by all offices. This evolutionary process, however, needs establishment of guidelines and scientific judgment on what level of sophistication is needed at the screening level to satisfy broad needs.

As more advanced information is required, standardized tests may not be possible because each act may require a specific type of information and all tests may not be equally applicable to all compounds. It may be possible to eventually evolve an EPA-wide progressive testing scheme based on informational requirements. Such a scheme would allow each office to specify the amount and type of information required to satisfy its needs in predicting environmental fate and transport. For example, in dealing with solid waste disposal, RCRA may require extensive characterization of the transport and fate of a chemical in soils, while CAA may involve little, if any, soil testing. The same parameters and screening tests for soils should be applicable to both FIFRA and RCRA. Although one office may require more detailed transport and fate parameters than another, the same testing schemes and methodologies should be applicable to both. The same basic information should be required to estimate the fate and transport of a chemical in water regardless of which EPA act or office requires the information. A generalized tier scheme would allow chemicals to progress to the more detailed tests required by the more stringent act.

There are a number of advantages to be gained by adopting one set of screening tests to estimate environmental fate and transport parameters of chemicals. The EPA could more efficiently review the tests on a periodic basis to insure that they are based on the best available methodology. Each EPA office would not have to develop and validate its own tests. Companies could more efficiently generate transport and fate parameters if they utilized common testing procedures at the initial screening level. The benchmark approach to evaluating test data would be easier to implement if a basic set of fate and transport data was available for a number of chemicals. The most significant environmental fate and transport routes can be easily identified from a complete base set of data.

The parameters required by each office should be based on the use, toxicity, manufacture, and volume of a new product. Products with low toxicity, intended for limited use, and with a low production volume, should not be required to undergo a full battery of tests. The cost of generating a complete and detailed set of transport and fate parameters would severely limit the development of new, low volume specialty chemicals. Sales of a highly effective, limited use product may not be sufficient to cover the cost of testing.

6.5 QUALITY ASSURANCE CONCEPTS

6.5.1 Introduction

Quality Assurance (QA) and Quality Control (QC) are terms frequently used as synonyms. It is proposed, for purposes of this report, that they be cast as the overall and specific components of systems to provide a high degree of confidence in test and experimental data (Kanzelmeyer 1977). Quality Assurance is a total system organized and designed to provide for accurate and precise results. Quality Control is specific action related to components of the system providing checks, controls, replicates, standards and calibrations suitable for statistical estimates of confidence in data elements.

Projecting guides will be used by a number of different facilities engaged in a variety of projects while QA Guidelines should cover all basic factors. However, the guidelines should be broad and flexible. The goal is to produce good, valid results. The means to the goal should not be confused with, or substituted for the end result or primary purpose: valid, accurate data. No one specific instrument, procedure, or requirement should be mandated unless it is the sine qua non for high quality results.

While the following QA components are most frequently applied to analytical chemistry, the basic elements are applicable to other areas and tests. Overall, the basis for most environmental work lay in analytical tests; thus, the emphasis on analysis. For example, in physicochemical parameters such as solubility, vapor pressure, K_{OC}, hydrolysis, photolysis and leaching the components in 6.5.2.1 through 6.5.2.5, and 6.5.2.7 are applicable with specific modifications to meet the specific parameter.

6.5.2 Quality Assurance Components - For Analyses

6.5.2.1 Personnel Requirements

In any quality assurance program, selection of personnel is a most important function. Administrators, directors, and supervisors should evaluate personnel on a continuing basis to determine whether they are thoroughly trained to perform the duties of the job they are assigned. The evaluation should include academic achievement, work experience, on-the-job training, workshops, and special courses. Certain levels of proficiency should be maintained through training programs for all employees due to the importance that their initial and continuing levels of competence enable them to perform at an acceptable level. However, overspecification and restrictive directions as to details must be avoided.

6.5.2.2 Procedures

All technical methods and laboratory procedures should be well-written and updated. A procedure manual should be maintained in the area where the testing is performed. As a general outline, the following are normal sections of a procedure.

1. Purpose

Principle use to include type of sample, purpose for testing, or an experiment and reason for procedure.

2. Summary

Include basic technique, range in concentration for which test is applicable, problems, interference, source of error and reference to a standard method which is equal or equivalent.

3. Safety

Include precautions for the particular method.

4. Apparatus

Listing to include type of instruments, wavelength specifications, ranges or any parameters critical or specific to the method being described. Illustrations are sometimes easier and clearer than lengthy descriptions.

5. Reagents, Standards, Media

Listing and/or preparation to include brand names where critical to procedure, purities, critical weights, nearest measurement units to which standards must be weighed or measured, concentrations, etc.

6. Calibrations and Standardization

Procedures to include graphs or tables if needed, temperature checks, limits of method if applicable.

7. Test Procedure

Detailed step-by-step procedure should be written exactly as performed; quality control measures can be included here or in a separate section. However, allowance must be made for exercise of scientific judgment and non-essential specifics avoided.

8. Calculations

All formulas must be listed as used and all variables described or defined.

9. Interpretation

Include critical values, significance of values, follow-up indicated by results.

10. Precision and Accuracy

Information regarding precision and accuracy of the method described should be included, i.e., published values determined by past experiences, internal experiments and collaborative testing. The source of the information should be noted.

11. References

Include sources of background information on the method itself, and any information that substantiates use of the method.

Although the above list appears all-inclusive, it serves only as a guide in preparing written procedures. Not all items are applicable to all procedures and they may be combined or rearranged as necessary. The procedure manual should be reviewed at least annually or at any time method changes or revisions occur. All approved changes or revisions must be documented.

6.5.2.3 Reagents and Standards

The quality of results depends to a great extent on the quality or purity of reagents and standards. The purity of chemical reagents varies from technical grade to ultra pure grades. The American Chemical Society Committee on Analytical Reagents has established criteria for certain chemicals which they label (AR) grade or (ACS) grade. These chemicals are of very high purity and should be used in all analyses in the laboratory, unless otherwise stated. The labels on the container should be checked and the contents examined to verify that the purity of the reagents meets the needs of the particular method involved.

Reagents must always be prepared and standardized with special care against reliable primary standards. They must be restandardized or prepared fresh as necessary to retain their stability. All reagents, standards and general chemicals should be labeled as to date of receipt, date opened, and expiration date.

Following are a few guidelines in the preservation and storage of reagents and standards:

1. Aqueous solutions should be stored in tightly closed glass or plastic bottles.
2. Colored aqueous solutions which are light sensitive should be kept in dark brown or amber bottles.
3. If reagents or standards require refrigeration, make labels or indicate on bottle that sample is to be refrigerated.
4. NEVER introduce pipettes into reagent or standard bottle.
5. Reagents and standards perform best when freshly prepared. Laboratory preparation of reagents and standards should indicate on the label the date of preparation and the initials of the person who prepared it. In some cases, it is a good idea to include the components of the solutions. Whenever special precautions are necessary, they should be mentioned under the reagent preparation and should be included on the label.

Water quality or purity is another parameter that should be given considerable attention in any analytical work. Distilled or demineralized water is used in the laboratory for dilution purposes, preparation of reagents, and rinsing glassware. High purity water has been defined as water that has been distilled and/or deionized so that it will have a specific resistance of 50,000 ohms (2.0 micromhos conductivity) or greater. Although ordinary distilled water is adequate for many analyses, specific methodology may require a further refinement or conditioning of the purified water.

Laboratory reagent water should be checked periodically for resistivity, trace metals, bactericidal properties, or any parameters which may influence test results. The procedures for the quality checks should be documented.

6.5.2.4 Laboratory Apparatus and Instruments

Familiarity with the equipment is necessary in order to produce valid data and involves not only the capabilities but also the limitations of the test equipment. Much of this information is received from the vendor when equipment is purchased. However, the analyst has the primary responsibility for maintaining the equipment. A preventive maintenance program should be established to insure peak performance of all equipment. This preventive maintenance program should be documented by keeping a ledger and/or visible posting on the equipment, the dates of preventive maintenance, as well as the due dates.

Each piece of measuring or test equipment should be calibrated on a scheduled basis using appropriate standards, as well as approved published practices. Regardless of the type of calibration or materials used, an effective quality assurance program requires accuracy levels of those materials that are consistant with the method of analysis. All of this information should be documented.

6.5.2.5 Sample Collection and Preservation

The quality of the sample in any experiment will control the results of the test. It is unfortunate that engineering miracles in automation and newer analytical methodology are generally unable to differentiate between a properly collected sample and one which is improperly collected. Therefore, it is essential that guidelines be instituted for the collection, preservation and transport of samples to the laboratory. The guidelines should include the following:

1. Type of specimen needed
2. Minimum sample size
3. Proper method or technique of collection including specific storage instructions
4. Container to be used - with amount and type of preservative, if any
5. Holding time.

A rejection policy should also be established specifically for those cases which do not meet the above criteria.

6.5.2.6 Analytical Quality Control

Good facilities, competent personnel, an up-to-date procedure manual, high purity reagents and standards, and the best in calibrated equipment do not automatically provide valid and reliable data. The basic requirements in any quality assurance program have to include the above conditions, however, the main ingredient used in determining validity and accuracy of results is analytical quality control.

Analytical quality control incorporates not only proved and acceptable methods, but analysis of a control sample (internal quality control or statistical quality control) and confirmation of the ability of a laboratory to produce acceptable results by requiring analysis of unknown reference samples (external quality control, proficiency testing, or laboratory evaluation).

Since most analytical errors in the laboratory are classified as determinate (traced to a particular problem) or indeterminate (statistical errors), it is possible to assess statistical data graphically by use of control charts. In order to monitor daily operations for accuracy and precision, data must be accumulated. Basically, the procedure is as follows:

1. Document all control values for a relevant period of time.

2. Determine the mean and standard deviation.

3. Reject values falling outside of ± 3 standard deviations.

4. Recalculate the mean and standard deviation.

5. Calculate the mean ± 2 standard deviations.

6. Establish the range of acceptable values.

Particular attention has to be given to the understanding and interpretation of these data and an action policy should be developed to determine the course of action taken when values are out of control. Some form of comparison or tabulation should be kept to evaluate results and detect trends.

Graphic display of control values provides a visible means of determining control limits, but it is not the most desirable method of quality control. One of the most efficient means of quality controlling analytical procedures is computerization. Many existing information processing systems are capable of producing such statistical parameters as frequency, range, mean, standard deviation, and coefficient of variation. Computers are able to store vast amounts of information with relative ease of retrieval. Many are designed to document or display control values on a regular basis and provide useful information when values are out of range or show a particular shift or trend. Computerization with automated and semi-automated equipment can effectively document and assess those statistical parameters necessary for the evaluation of the testing systems. Even though the computers will perform much of the data analysis and print results in report form, this information has to be interpreted by laboratory personnel.

An external system of audits and checks is another aspect of quality control involving both real and simulated specimens. Proficiency testing can assist the laboratory in determining whether the values it reports are comparable to those of other labs when using the same or similar methods. In many laboratories, in-house values are subject to subtle changes from time to time and these changes are not recognizable without the use of some external source of reference. Well-run proficiency testing programs serve to complement the daily quality control program and also provide motivation for better laboratory performance. Proficiency testing samples should not be treated as special tests, but should be handled as a part of the routine work load. If the laboratory considers its routine performance so poor as to require special handling, then it has more problems than could be corrected by a proficiency testing program.

There are a number of areas in the laboratory where the final decision of an analysis or series of analyses is based on the education and experience of the analyst and not on a quantitative measurement. Because of the subjective nature of the work, sound scientific judgment, consultation with colleagues and supervisors, and a modification of techniques and procedures may often be required. The final results in many instances are based on comparisons. Conditions leading to the final results should be controlled and documented. The quality control aspects of non-quantitative data justify careful observation and proper documentation of observations in order to support conclusions.

6.5.2.7 Definitions (Mandel 1977)

Quality Assurance - Program designed to assure required accuracy and precision of results. Included are selection of proper methods, tests or operations, quality control, selection of limits, evaluation of data, and qualifications and training of personnel.

Quality Control - Specific actions required to provide data for the Quality Assurance program. Included are standardizations, calibration, replicates and check samples as part of a specific test procedure or specific procedures for a given area or function which supports one or more test methods.

Accuracy - The closeness of a test result to the expected value.

Precision - Reproducibility of test results.

Standard Deviation - A measure of the average dispersion from the arithmetic mean value:

$$SD = \sqrt{\frac{\Sigma(X_1 - \bar{X})^2}{N - 1}}$$

Where:

Σ = "Sum Of"

X_1 = Value of Single Determination

$\overline{X}$ = Arithmetic Mean of N Determinations

N = Number of Determinations

Arithmetic Mean - The sum of all observations divided by the number of observations:

$$\overline{X} = \frac{\text{Sum of Observations}}{\text{No. of Observations}}$$

Coefficient of Variation - Standard deviation expressed in terms of the percentage of the mean:

$$CV = \frac{SD}{Mean} X\ 100$$

Range - The interval between the highest and lowest figures in a related series of data.

Frequency - Magnitude of occurence.

Determinate Errors - Those errors which originate from sources such as malfunctioning instruments, incorrect operations, inappropriate temperature setting, glassware, contaminated chemicals, and human errors.

Indeterminate Errors - Those errors which are inherent in any testing system and are not traceable to any particular problem.

Primary Standard - A substance whose concentration or purity is known - usually 99% or better.

Linear Regression - Statistical technique used to determine the relationship between two variables, one of which is known with a certain degree of accuracy and the other is predicted by fitting the variables to a line equation rather than plotting and visually estimating that equation.

6.6 CONCEPT OF BENCHMARK CHEMICALS

Only in recent years have serious attempts been made to correlate laboratory observations on the fate and transport of chemical substances to their actual behavior in the environment. In part, the delay in undertaking such studies was due to the complexity and variability inherent in the biochemical systems under investigation and a lack of standard methodology that could yield a more unified, scientific approach. The lack of a unified approach has limited the ability of environmental chemists and regulatory agencies to confidently predict and correlate the environmental fate and transport of one chemical substance with that of another. In the case of pesticides, which are used as examples since they have been more thoroughly studied, meaningful environmental chemistry should be conducted to provide relevant information on their behavior and significant dissimilation products in the environment. This will allow judgment to be made of their potential impact on the environment when they are to be used on a large scale.

Prior to the introduction of an experimental pesticide on a large scale, it is suggested that a judgment on its potential fate and transport in the environment be constructed by comparing results generated by suitable protocols for the experimental pesticide with those obtained for a "benchmark" pesticide chemical currently or previously in large scale use. It is understood that the environmental behavior of these benchmark chemicals has been observed or measured in numerous laboratory and field studies and it has been judged acceptable or unacceptable relative to specific types of end uses. Such an approach has been briefly described by Hamaker (1972) and Goring (1972) for pesticide degradation in soil and for all other aspects of pesticide behavior in the environment, respectively.

Using the example of an experimental pesticidal chemical, the sequence of events in the "benchmark" chemical concept may be described in the following:

1. Define the most important properties of the pesticide that determine its behavior in the environment, e.g. volatility, Kp, adsorption, reaction rates.

2. Develop laboratory methods to accurately and precisely measure these properties.

3. Measure these properties for the major "benchmark" chemicals currently being used or for those "benchmark" chemicals that had been used on a very large scale for many years and for which a large body of information is available.

4. Establish the relationship between the laboratory (greenhouse and small-scale field studies included when available) measurements and field behavior for the "benchmark" pesticides.

5. The potential environmental fate and transport of an experimental pesticide chemical could then be predicted by comparing the data with those accumulated for "benchmark" chemicals. This may be done by the use of mathematical models.

The utility of this "benchmark" approach is that it provides a rational matrix of information on the environmental behavior of pesticides that increases in scope, depth and usefulness as each new experimental pesticide is incorporated into its proper place in the matrix. This concept of "benchmark" chemicals may be fine-tuned relative to its structure-activity and predictive value as more information becomes available on the various aspects of environmental fate and transport for specific chemicals.

A list of suggested "benchmark" pesticides is given in Table 6-2. Selection of these pesticides was based both on wide usage over a long period of time and on an overall range of their properties that encompass the extremes of behavior likely to be encountered. In a few cases, chemicals were selected for their unique physicochemical properties or their environmental behavior patterns. It is hoped that additional "benchmark" pesticides will be added to this list as the need arises. The final list should be representative of other pesticide classes and uses such as fumigants, aquatic pesticides, and repellents. This concept is not limited to a given class of chemicals such as pesticides but may also include all environmental chemicals including the naturally-occurring compounds.

In support of the "benchmark" concept, a suggested classification matrix for pesticides is provided in Table 6-3. It is important not to consider this matrix as all-encompassing but merely as illustrative of the kind of experimental data which should be considered in predicting the fate and transport of chemicals in the environment. For a more complete understanding of the environmental fate and transport of chemicals, one should add data requirements to improve the predictability of the benchmark concept using various tiers of testing as required by appropriate criteria. For example, the described experimental parameters are not applicable to cationic chemicals.

Although this section does not include the effect of chemical substances on the target and non-target organisms, the benchmark chemical concept may also incorporate toxicological parameters to be used as a tool to predict potential structure-toxicity hazards.

It is hoped that continual improvements in the data presented in tables 6-2 and 6-3 will be achieved by the promotion and constant validation of this approach via data generated by all scientists, e.g., industrial registration data, data generated by regulatory agencies, and published literature reviews and information. In order to fill the data gaps and to improve the usefulness of this approach, additional research should be conducted (research grants, contracts by government agencies) on chemicals which may have little or no economic significance.

6.6.1 Utilization of the Benchmark Approach

The following elaboration of the process of developing the benchmark concepts and data indicate activities that reflect the utility of the approach:

1. Determine the most important properties of chemicals substances that best determine their environmental fate and transport.

2. Determine which of these properties can be measured by conducting laboratory and greenhouse experiments.

TABLE 6-2 SUGGESTED BENCHMARK CHEMICALS

Chemical Class	Pesticides*
Aliphatic acids	Dalapon
Aniline-based	Chlorpropham, Alachlor
Benzoic Acids	Dicamba, Chloramben
Carbamates	Carbaryl, Carbofuran, Methomyl
Dinitroanilines	Trifluralin
Fumigants	DBCP, 1,3-D, Methyl bromide
Organochlorines	DDT, Lindane, Dieldrin
Organometallics	MSMA
Organophosphates	Parathion, Malathion, Diazinon, Methyl Parathion, Phorate, Fensulfothion, Chlorpyrifos
Phenols	Dinoseb
Phenoxyalkanoic acids	2,4-D, 2,4,5-T
Phthalamides	Captan
Picolinic acids	Picloram
Thiocarbamates	EPTC
Triazines	Atrazine
Ureas	Diuron, Fluometuron
Miscellaneous	Dichlobenil, Benomyl

*Common Names

TABLE 6-3. SUGGESTED CLASSIFICATION MATRIX FOR CHEMICALS (GORING 1972).

Biological, Chemical, or Physical Characteristics	Numerical Range				
	Very High	High	Medium	Low	Very Low
Soil Independent					
A. Water solubility (ppm)	>1000	100 - 1000	10 - 100	0.1 - 10	<0.1
B. Vapor pressure (mm Hg)	$>10^{-1}$	$10^{-1} - 10^{-3}$	$10^{-3} - 10^{-5}$	$10^{-5} - 10^{-6}$	$<10^{-6}$
C. Hydrolysis (days, t1/2 at pH)	>100	25 - 100	5 - 25	1 - 5	<1
D. Photolysis (days, t1/2 pesticide)	>100	25 - 100	5 - 25	1 - 5	<1
E. Water/Air ratio*	$>10^7$	$10^5 - 10^7$	$10^3 - 10^5$	$10^2 - 10^3$	<100
F. Octanol/Water ratio (K_p)	$>10^6$	$10^5 - 10^6$	$10^3 - 10^4$	$10^2 - 10^3$	<100
Soil Dependent					
G. Soil/Air ratio*	$>10^7$	$10^5 - 10^7$	$10^3 - 10^5$	$10^2 - 10^3$	<100
H. Adsorption Coefficient (soil/water ratio, K_{oc})	$>10^4$	$10^3 - 10^4$	$10^2 - 10^3$	$10 - 10^2$	<100
I. Leaching (TLC R_f)	1.0 - 0.90	0.89 - 0.65		0.34 - 0.10	0.09 - 0
J. Soil persistence (mo. to 1/2 dissipation)	>12	6 - 12		0.5 - 2	<0.5

3. Collect and review all available research data (literature review, data generated by the EPA and data, if available, in EPA files) on the environmental fate and transport of chemicals that have been introduced, used, or are naturally present on a significantly large scale over a long period of time. This part of research should collate the laboratory (greenhouse) data and the field data separately.

4. Determine if existing laboratory or greenhouse methods accurately and precisely indicate the environmental fate and transport parameters. Additional research may be necessary to improve the experimental methodology.

5. Select benchmark chemicals based on their structure-reactivity, wide and long-term usage, and for unique characteristics.

6. Establish the relationship between the laboratory (greenhouse) measurements and the environmental behavior for the selected benchmark chemicals.

7. Using the previously obtained structure-reactivity relationships, calculate the expected environmental fate and transport of a new chemical substance under investigation and then, through appropriate regulatory treatment, propose its "expected environmental profile", (i.e. first or second tier assessment of expected environmental fate and transport).

8. The true validation of the structure-reactivity benchmark chemicals concept is realized when the new chemical is subjected to field testing under actual use conditions.

9. These new field data on the new chemical should then be fed back to confirm the predictive value of the benchmark chemicals concept.

10. Benchmark chemical concepts may be extended to structure-toxicity relationships where the necessary data are available.

6.6.2 Limitations of Benchmark Chemical Concept

The structure-reactivity concept emphasizes pesticides and within that class of compounds (based on use) cationic compounds are exceptions because of their unique chemistry. Because of this exception and because the concept has not been fully validated, there is reason to believe that it may not be useful in every case. Therefore, it is mandatory to make certain that scientific judgment prevails at all levels of assessment (environmental fate and/or risk assessments) while dealing with a new compound.

The benchmark concept gives primary considerations to pesticidal chemicals. It should be noted that due to differences in the properties and quantity of chemicals regulated under different laws, the utility and application of the benchmark concept will differ under the various acts such as the Clean Air Act, Clean Water Act, and Resource Conservation of Recovery Act, as compared to that for TSCA and FIFRA.

In attempting to predict the environmental behavior of a new compound by the use of the benchmark concept, one must use a probability approach coupled with mathematical modeling. The benchmark concept and mathematical modeling, until further refined and validated, cannot be expected to precisely predict the environmental fate of an experimental chemical. Instead, it serves to provide a profile of transport and fate behavior and to focus attention on more important and pertinent tests that must be conducted to more accurately elucidate the fate and transport of a chemical in the environment.

6.7 DISCUSSION

There are a number of federal laws dealing with pollution that involve regulation of chemicals (Federal Water Pollution Control Act, Clean Air Act, Resource Conservation and Recovery Act, Federal Insecticide, Fungicide and Rodenticide Act, and Toxic Substances Control Act). With respect to chemicals, the basic objective in each of these acts is to prevent any significant adverse effect on man and the environment which requires attention be given to manufacture, transport, use, and disposal of chemicals. Once in the environment, the chemical may be transported by natural processes and may directly contact man or other biota. The amount and distance transported under given conditions will be dependent upon the persistence of the chemical or its fate in the environment. Therefore, regulation of chemicals to achieve the objective of human and environmental protection requires adequate knowledge of transport and fate of the chemicals. This section of the report is concerned with research needs on transport and fate of chemicals to allow effective and rational implementation of laws. In addition, there is need for concern for development of testing protocols, quality assurance of tests, and appropriate application of tests to acquire relevant information.

Though a number of laws are concerned with the regulation of chemicals, the extent of this concern and requirement varies markedly from law to law. The Toxic Substances Control Act and the Federal Insecticide, Fungicide, and Rodenticide Act deal with chemicals from manufacture to ultimate disposal while the Drinking Water Act and others have a more narrow spectrum of interest. However, to the extent that regulation is required under an act, basic information on transport and fate is necessary for proper implementation of the regulations. Fundamental information that indicates the propensity of the chemical for transport and persistence should be identified by appropriate research. The present development of the field of chemodynamics indicates that such physicochemical parameters as solubility, partition and distribution coefficients, and certain fundamental reactions may serve as a basis for predicting, at least to a first approximation, the probable transport, fate, and environmental distribution of chemicals.

The large number of chemicals with which the laws must be concerned precludes the detailed individual attention and data collection that would come from field trials and monitoring data. Therefore, chemodynamics and the "benchmark chemicals" approach utilizing laboratory measurements are needed and appear feasible (Goring 1972). Additional research should be conducted by EPA to ascertain whether there may be broader application of this approach to give a first level assessment of transport and fate.

In order to prevent significant adverse effect on man and the environment, the same amount of information will not be required on all chemicals. By virtue of the properties of the chemical, method of use, and other considerations, it will be possible to identify low hazard compounds . The most economical course of action would be to develop a multi-tier system of data requirements. Thus, the first tier of requirements may be for basic physical-chemical data obtained in laboratory studies with appropriate interpretation and predictions derived from the data. Using the benchmark chemical technique, estimates of probable biological activity and persistence may indicate more elaborate biological testing is necessary. Depending upon the physical and biological properties of the compound, the amount to be produced, and the method of use, more elaborate requirements would be established for the successive tiers of testing. The ultimate goal would be the development of a mathematical model that would give reasonable estimates of the transport, distribution, and fate of such a chemical. However, current mathematical models have not been developed that permit such assessments and such models should not be expected to be forthcoming in the future without further research.

In devising appropriate regulatory action, the ability to identify and measure the subject compound is essential. Therefore, the development of analytical methods of appropriate sensitivity, precision and reliability is important. The same may also be said of the various other tests to determine the physical and biological properties of the compound. It is important, therefore, that such tests and analytical methods be developed and a suitable protocol of quality assurance be a part of the program.

6.8 RECOMMENDATIONS

A vigorous program of research on transport and fate is needed to regulate chemicals and prevent significant adverse impact on man and the environment while allowing for the orderly and expeditious development of needed chemicals. The development of the appropriate basic information for interpreting and prediciting the transport and fate of chemicals is needed for implementation of the current and future laws and regulations.

There are also a number of natural and anthropogenic chemicals in the environment. These may mask or interfere with the detection or monitoring of some chemical of future interest. The background levels of a number of chemicals should be identified and quantitated. This information is for the purpose of knowing what is in the environment, the possible significance of the presence of a given chemical, and to avoid confusion of this chemical with some similar but new product.

Research should be supported to develop further basic tests to provide improved scientific information on transport and transformation and expand the basis on which predictions may be made.

Appropriate generic test protocols as well as benchmark chemical approaches should be developed and implemented in order to deal with the large number of chemicals covered by the various acts.

The role of biota including man should be recognized as a factor in transport and fate and cognizance be taken of the role of the interaction of physiological, genetic, and population composition changes in the fate of the chemicals.

Appropriate tier test protocol development should be a priority activity to facilitate assessment of chemical hazards. The tier test protocols should take cognizance of the amount of chemical, toxicity, the manner of use, and propensity for transport. Such tier testing would allow the most attention to be given to the materials posing the greatest hazard to man and the environment.

Where mathematical models are to be used for a basis of regulation, research should be undertaken to develop more accurate and reliable holistic models. These models should take into account the multimedia aspects of transport and fate and should involve "sensitivity analyses" and temporal and spatial relationships. Valid multimedia exposure models or linked single compartment models are needed to assist in rapid, consistent exposure assessment of new chemicals.

Methodologies are needed for screening new chemicals for risk assessments based on environmental transport and fate considerations. EPA will have a limited amount of time to assess the risk posed by proposed use, manufacturing, processing, distribution, and disposal activities and needs decision criteria by which it can focus resources on potentially high risk chemicals.

A qualitative ranking or profile of the relative importance of the various environmental transport and persistence parameters is needed. This ranking should be based on monitoring data interpreted in comparison with results of laboratory environmental fate studies and microcosm studies. Testing and risk assessment resources should focus on the most important environmental fate parameters, emphasizing the more minor parameters only where structure-reactivity relationships and other factors indicate the need.

Decision criteria should be developed for testing and risk assessment. Such testing criteria will indicate when testing is necessary and what types of tests should be performed. These criteria may be based on results from simple tests, structure-reactivity relationships, etc. The risk assessment criteria referred to are those to be used at the end of the risk assessment process after the screening phase.

Development of more cost effective screening tests and more research on structure-reactivity relationships for new chemicals needs to be undertaken. The economics of new chemical development is such that testing costs should be kept minimal.

EPA requirements in regulations for test methods and procedures should be broad and flexible. The goal is to produce good, valid results. The means should not be confused with the goal or substituted for valid, accurate data suitable for its intended purpose or use. No one specific instrument, procedure, or test related requirement should be mandated unless it is the sine qua non for high quality results.

There is an urgent need for research and development of analytical and test methods which are suitable and practical for routine use in monitoring and control functions for compliance with regulatory aspects. The goal should be availability of accepted, practical valid methods at the time maximum contaminant levels or similar requirements are proposed. An effort is also needed to establish a reliability assessment system to consolidate the variability of all test data, and other data into a reliability estimate of conclusions or decisions such as the Department of Defense Reliability Programs.

The Regulatory Group participants are listed in Table 6-4.

TABLE 6-4. REGULATORY GROUP PARTICIPANTS

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Federal Insecticide, Fungicide and Rodenticide Act, 1972

Federal Water Pollution Control Act, 1972

Occupational Safety and Health Act, 1970

Resource Conservation and Recovery Act, 1976

Safe Drinking Water Act, 1974

Toxic Substances Control Act, 1976

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